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of Engineers
Waterways Experiment
Station

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August 1996

Strategic Environmental Research and Development Program

Proceedings of the 2nd Annual Site Characterization and Analysis Penetrometer System (SCAPS) Sensor Development Workshop

29-30 August 1995,
Vicksburg, Mississippi

by Ernesto R. Cespedes, Diane M. Cargile

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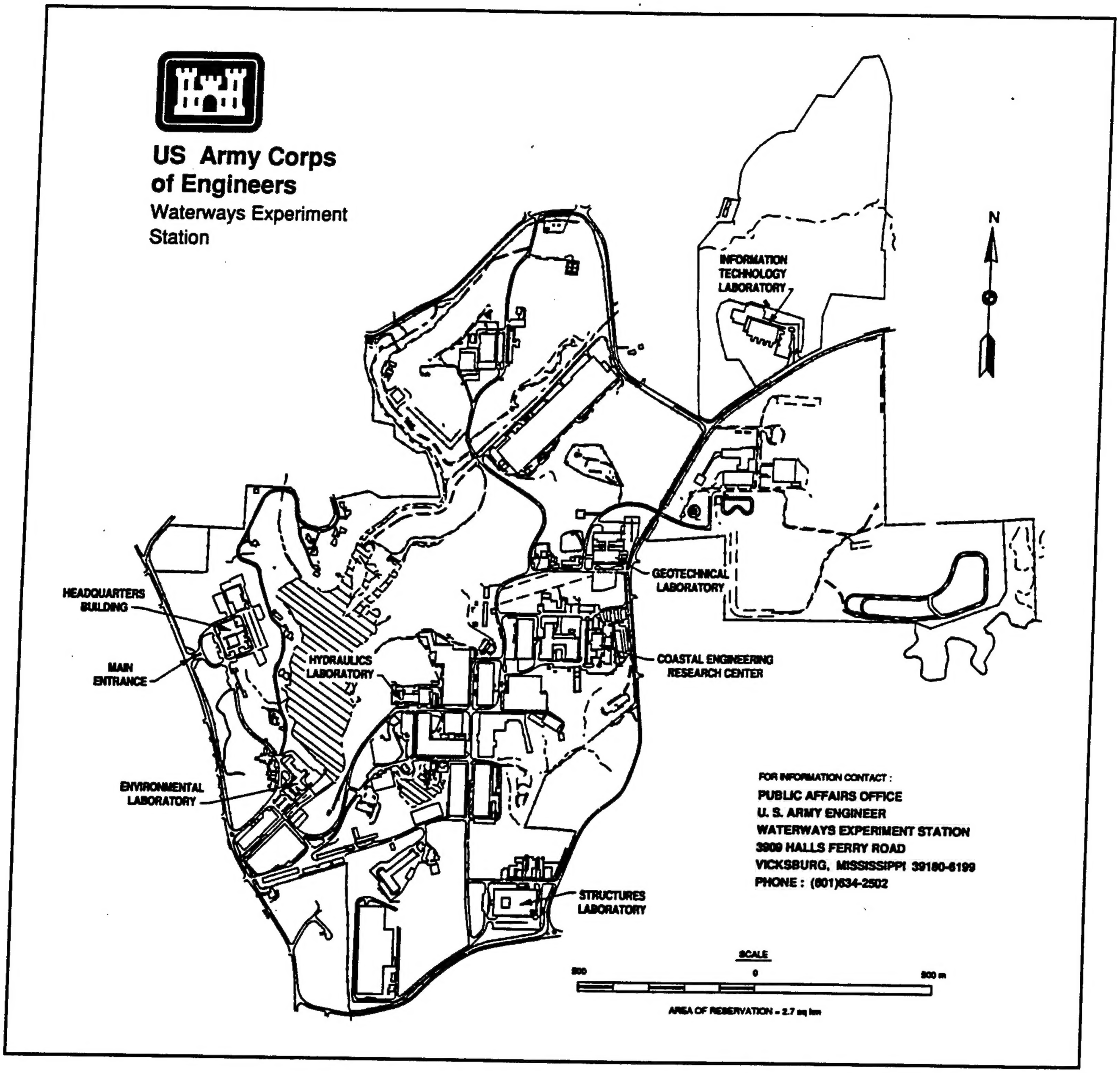
SERDP
Strategic Environmental Research and Development Program
Improving Mission Readiness through Environmental Research

Prepared for Headquarters, U.S. Army Corps of Engineers



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Contents

Preface

The 2nd Annual Site Characterization and Analysis Penetrometer System (SCAPS) Sensor Development Workshop was held at the U.S. Army Engineer Waterways Experiment Station (WES) on 29-30 August 1995. The workshop was sponsored by the Strategic Environmental Research and Development Program (SERDP), Washington, DC, under Project Number 94-729, "Accelerated Tri-Services SCAPS Sensor Development." Dr. John Harrison is Acting Executive Director, SERDP.

The workshop was organized and coordinated by Dr. Ernesto R. Cespedes, Environmental Engineering Division (EED), Environmental Laboratory (EL), WES, with the assistance of Ms. Diane M. Cargile, EED. This report on the proceedings of the workshop was compiled and prepared by Dr. Cespedes and Ms. Cargile.

This report was prepared under the general supervision of Mr. Norman R. Francingues, Chief, EED, and Dr. John W. Keeley, Director, EL.

At the time of publication of this report, Dr. Robert W. Whalin was Director of WES. COL Bruce K. Howard, EN, was Commander.

This report should be cited as follows:

> Cespedes, E. R., and Cargile, D. M. (1996). "Proceedings of the 2nd annual Site Characterization and Analysis Penetrometer System (SCAPS) sensor development workshop, 29-30 August 1995," Miscellaneous Paper SERDP-96-2, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

1 Introduction

Background

The Site Characterization and Analysis Penetrometer System (SCAPS) is receiving wide acceptance as a versatile tool for rapid subsurface screening of contaminated sites. Since the fielding of the first SCAPS vehicle at the U.S. Army Engineers Waterways Experiment Station (WES) during 1990, the Tri-Service SCAPS fleet has grown to seven vehicles (four Army and three Navy). In addition, the Department of Energy operates two SCAPS vehicles, and private contractors, under licensing agreements, operate a number of SCAPS technologies that support DoD, DOE, and EPA site characterization efforts.

The SCAPS platform consists of a 20-ton truck equipped with vertical hydraulic rams capable of pushing a cone penetrometer into the ground at a speed of 2 cm/sec to depths of over 50 m in nominally consolidated, fine-grained soils. During a push, SCAPS is capable of collecting subsurface stratigraphy data with spatial resolutions of 2 cm, as well as chemical contaminant data by means of sensors and samplers incorporated into the penetrometer head. The primary application of SCAPS technology has been to characterize sites contaminated with heavy petroleum, oils, and lubricants (POLs) by means of a laser induced fluorescence (LIF) sensors (Lieberman et al. 1991). Successful fielding of the LIF technology led to increased interest in expanding SCAPS capabilities to address other contaminants (Cespedes et al. 1994)

In 1994 the Strategic Environmental Research and Development Program (SERDP) funded a Tri-Service effort to accelerate the development and testing of advanced sensors and sampling technologies for SCAPS to allow characterization of sites containing explosives, metals, volatile organic compounds (VOCs), light POLs, and radioactive wastes (SERDP 1995). During the 1994 SERDP Program Review, the Scientific Advisory Board requested that a peer review panel be set up to monitor the progress of the sensor development project. It was also requested that yearly meetings be held that included the peer review panel, the Tri-Service developers, and the SCAPS users. The first meeting was held during 16-17 August 1994 and was expanded to include DOE and EPA researchers and users. This report describes the second

meeting which was held during 29-30 August 1995 at the U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.

Objective

The primary objective of this workshop was to have the Peer Review Panel evaluate the progress of the SCAPS sensor development project during the previous year and to have them recommend changes or re-directions of the research effort. In addition, the workshop provided an open forum for discussion of ongoing sensor development activities related to SCAPS within the Tri-Service, DOE, and EPA, with the goal of fostering partnering between agencies and reducing any duplication of effort. Lastly, the workshop provided an opportunity for SCAPS managers and users to evaluate ongoing research and to provide feedback to the sensor developers.

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4 Agenda

SCAPS Sensor Development Workshop
29-30 August 1995
USAE Waterways Experiment Station
3909 Halls Ferry Road
Vicksburg, Mississippi

Tuesday, 29 August 1995

0830 Welcome . . . . COL Howard (WES Commander)

0835 Overview . . . . Dr. Keeley (Env. Lab Director)

0845 Introduction of SERDP Panel Membership . . Dr. Cespedes (WES)

0900 Project Description/Status . . . . Dr. Cespedes

0915 SERDP Program Research Areas . . . . Dr. Cespedes

I. Laser Induced Breakdown Spectroscopy(LIBS) . . . Dr. Cespedes
Dr. Miziolek (ARL)
Mr. Theriault (NRaD)

II. Laser Induced Fluorescence Sensors

A. POL . . . . Dr. Lieberman (NRaD)
Mr. Nielsen (USAF/AL)

B. Explosives . . . . Dr. Cespedes
Dr. Sausa (ARL)

1045 Break

1100 III. Fiber Optic Raman Sensors . . . . Dr. Boss (NRaD)
Mr. Nielsen

IV. Electrochemical Sensors

A. Explosives . . . . Dr. Cespedes
B. VOC . . . . Dr. Davis (WES)

V. Spectral Gamma Probe . . . . Mr. Register (WES)

1230 Lunch

1315 VI. Sampling Technology . . . . Dr. Brannon (WES)
Dr. Davis
Mr. Leavell (WES)

VII. Data Processing Methodologies . . . . . . Mr. Goodson (WES)
VIII. Technology Demonstration/Implementation . . . . . Dr. Davis
Mr. Drinkwine (MRK, COE)
Dr. Lieberman

1500 Break

1515 User Needs . . . . SCAPS Managers & Operators
(ARMY, Navy, DOE, EPA)

1630 Adjourn

Wednesday, 30 August 1995

0830 Conclusions and Recommendations . . . . SERDP Panel

0915 DOE/EPA/DoD Related Research

A. On-Line Organic Sampler . . . . Dr. Doskey (ANL)
B. Moisture and Pore Pressure Sensors . . . . Dr. Knowlton (SNL)
C. Fiber Optic IR Sensor . . . . Dr. Aggarwal (NRL)

1000 Break

1015 DOE/EPA/DoD Related Research (Continued)

D. X-Ray Fluorescence Sensor . . . . Dr. Elam (NRL)
E. New Coring Device . . . . Mr. Lien (EPA)
F. Field Portable LIBS . . . . Dr. Cremers (LANL)
G. Direct Sparge Sampler . . . . Dr. Davis
H. Optical Sensors . . . . Dr. Vo-Dinh (ORNL)

1130 DOE/DoD Coordination and Collaboration . . . . All

1200	Lunch	
1300	Tour of SCAPS Truck	Mr. Konecny (WES)
	3-D Visualization Demonstration	Mr. Goodson
	ITMS Demonstration	Dr. Davis
1430	Adjourn	

5 Abstracts, Papers and/or Presentation Materials

The following three chapters contain briefing materials submitted by the workshop presenters and are printed as submitted with no editing. Although varied in format, the materials in this section represent a good summary of the workshop. In addition to the presentations and discussions described in this report, the workshop included demonstrations of SCAPS prototype probes and samplers, of the SCAPS 3-D visualization software, and of the modified hydraulic equipment in the WES SCAPS truck.

Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
cubic feet	0.2831685	cubic meters
Fahrenheit degrees	5/9	Celsius degrees or kelvins[1]
feet	0.3048	meters
inches	0.0254	meters
pound (force) inches	0.1129848	newton meters
miles (U.S. statute)	1.609347	kilometers
pounds (force) per square foot	47.88026	pascals
pounds (mass)	0.4535924	kilometers

[1] To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use this following formula: C=(5/9) (F-32). To obtain kelvin (K) readings, use: K=(5/9) (F-32) + 273.15.

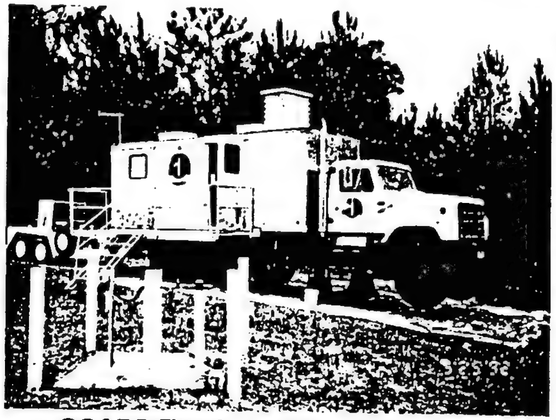
PROJECT DESCRIPTION

- SCAPS project is a fully coordinated Tri-Services effort to significantly accelerate the development, testing, and demonstration of sensor and sampler technologies to enhance the capabilities of SCAPS to detect and map subsurface contaminants in situ

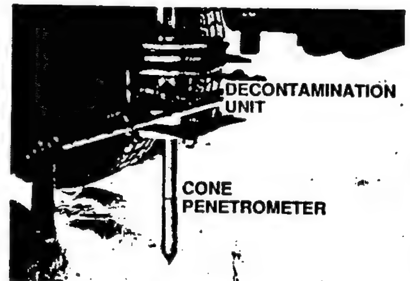
TECHNICAL OBJECTIVES

- Accelerate the development, testing, and demonstration of the following SCAPS technologies:
  - I LIBS - metals
  - II LIF - POLs, explosives
  - III FORS - VOCs
  - IV Electrochemical sensors - VOCs, explosives
  - V Spectral Gamma Probe - radioactive wastes
  - VI Sampling
  - VII Data processing

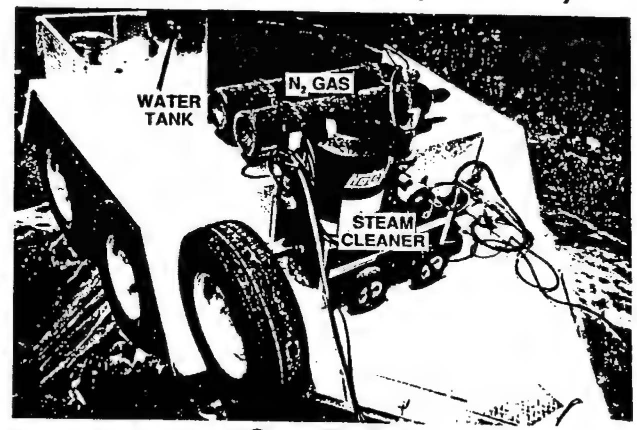
SITE CHARACTERIZATION AND ANALYSIS PENETROMETER SYSTEM (SCAPS)



SCAPS Truck and Grout Trailer
(Monitoring Well in Foreground)

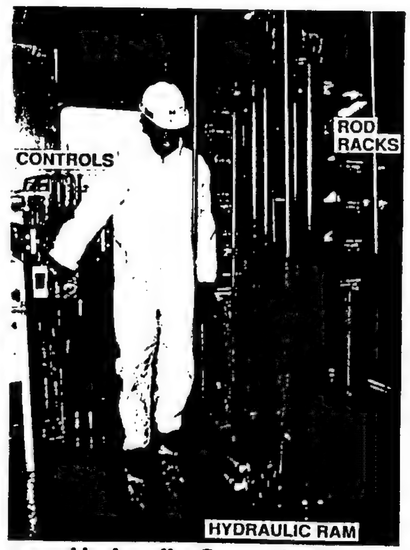


Cone Penetrometer
With Sensor Package

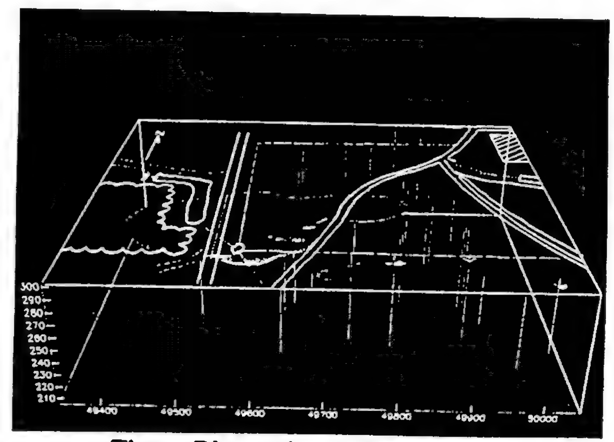


Grout Trailer

Data Acquisition/Processing
Compartment



Hydraulic Operations
Compartment



Three-Dimensional Contaminant
Visualization

TECHNICAL APPROACH

SERDP
A Partnership to Improve the Environment

S•C•A•P•S

- **Select candidate sensing technologies**
  - Appropriate for DoD, DOE, EPA contaminants of interest
  - Potential for rapid, in situ applications
  - Implementable in SCAPS
- **Develop laboratory instrumentation to evaluate technology**
  - Soil matrix effects
  - SCAPS implementation considerations
  - Detection limits
- **Develop associated support technologies**
  - Data acquisition hardware / software
  - Scientific visualization
  - Data analysis
- **Develop prototype SCAPS sensor probe**
- **Conduct laboratory / field tests**
- **Conduct demonstration of new SCAPS sensor systems**

TECHNICAL APPROACH

SERDP
A Partnership to Improve the Environment

S•C•A•P•S

- **Contaminants**
  - Explosives
  - POLs
  - VOCs / Solvents
  - Heavy Metals
  - Radionuclides
- **Sensor Technology**
  - LIBS
  - LIF
  - Photofrag. / LIF
  - FORS
  - Electrochemical
  - Spectral Gamma
- **Sampling Technology**
  - Thermal Desorption
  - Multiport Sampler
- **Data Processing**

→ **Demonstration → Transition**

TECHNICAL APPROACH

- **Exploit technological advances**
  - Fiber optics
  - Solid state tunable lasers
  - Diode lasers / arrays
  - Detector technologies
  - Computer hardware
  - Developments in the field or laser applications to chemical analysis

TECHNICAL RISKS

- **Transition of laboratory methods to operational (field use) technology**
- **Performance variability of in situ sensors with site-specific conditions**
  - Soil matrix
  - Interferences
  - Contaminant mix
  - Contaminant state

PERFORMERS

- **Lead Lab - U.S. Army Engineer Waterways Experiment Station**
- **Technical POC - E. Cespedes**
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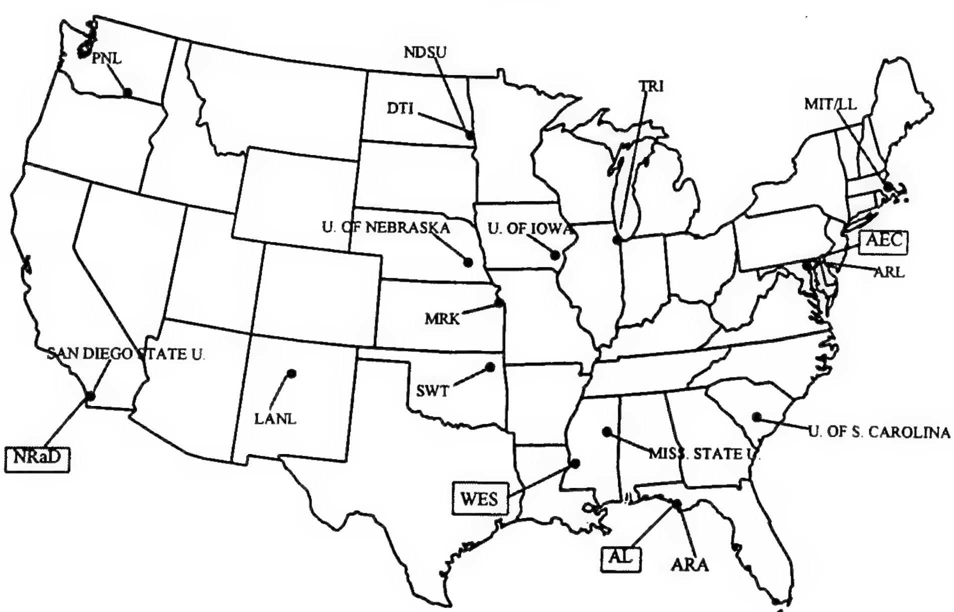
  - University of South Carolina
  - University of Nebraska-Lincoln
  - Mississippi State University
  - University of Iowa
  - MIT/LL
  - Transducer Research, Inc.
  - Los Alamos National Laboratory
  - Naval Research Laboratory
  - Others TBD

PERFORMERS



HIGHLIGHTS

- **New prototype SCAPS probes**
  - Explosives
  - Thermal desorption VOC sampler
  - Electrochemical VOC probe
  - FORS probe
- **Demonstrated 3-D visualization in field**
- **Successful LIF demonstrations involving EPA, WGA**

FIELD TESTS / DEMONSTRATIONS

PAST PERFORMANCE

	FY93	FY94	FY95
Technical Papers	3	2	>15
Conference / Symposium Presentations	7	9	>20
Technical Reports	1	1	2
Patent Disclosures / Applications	1	2	1
CRADAs	0	1	1
Licensing Agreements	0	2	0

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DoD EPA DOE

RESEARCH AREA I
LIBS SENSOR

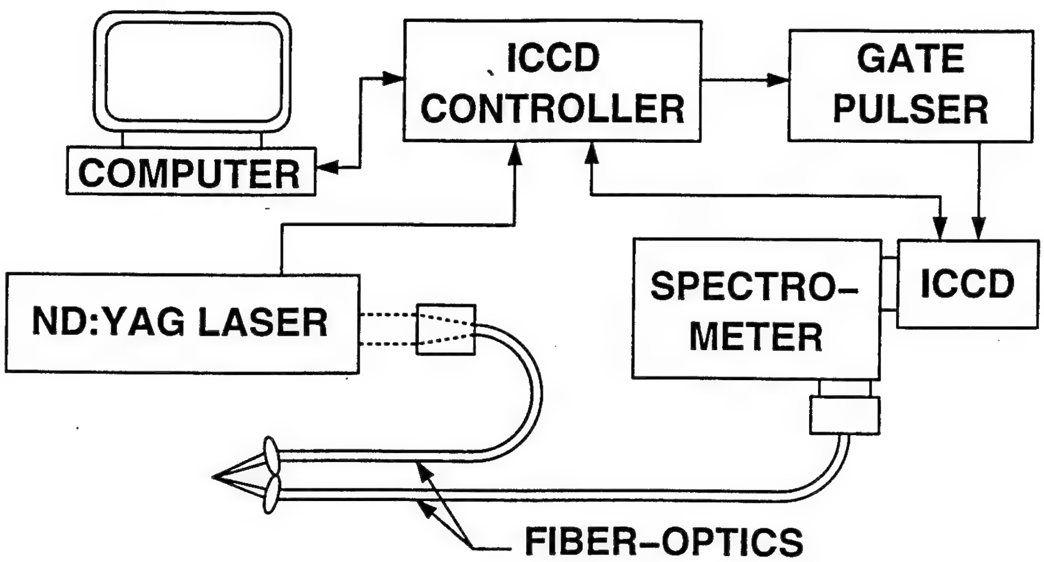
S•C•A•P•S
Site Characterization and Analysis Penetrometer System
Tri-Service Army Navy Air Force

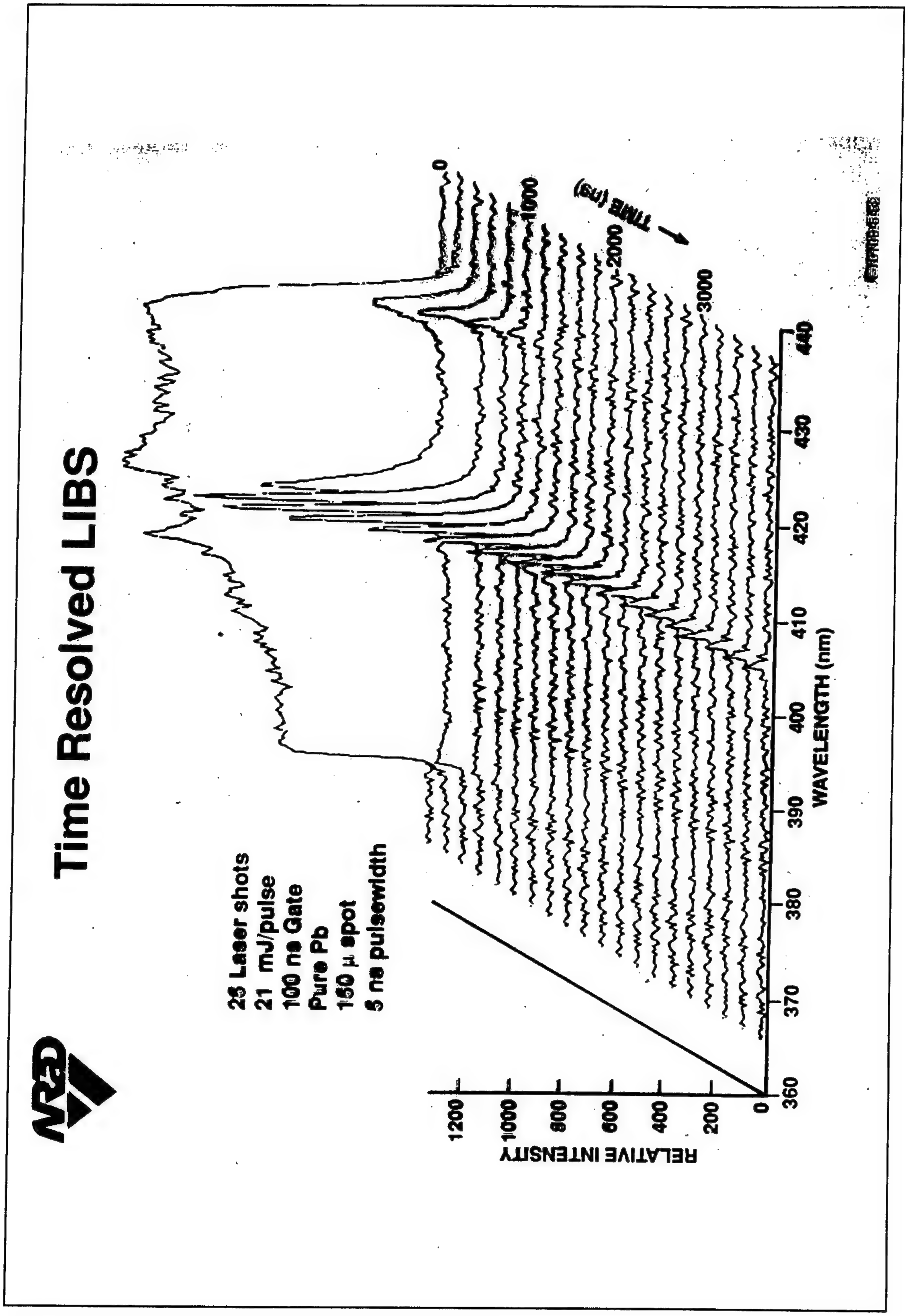
Milestones	Schd	Reschd	Comp
• Complete characterization of optical fiber	06/94	09/94	09/94
• Complete laboratory prototype F.O. LIBS system	09/94	10/94	10/94
• Complete design of prototype LIBS probe	09/95		
• Complete LIBS software development	11/95		
• Complete fabrication of LIBS prototype probe	03/96		
• Complete field tests / demonstration of LIBS system	12/96		

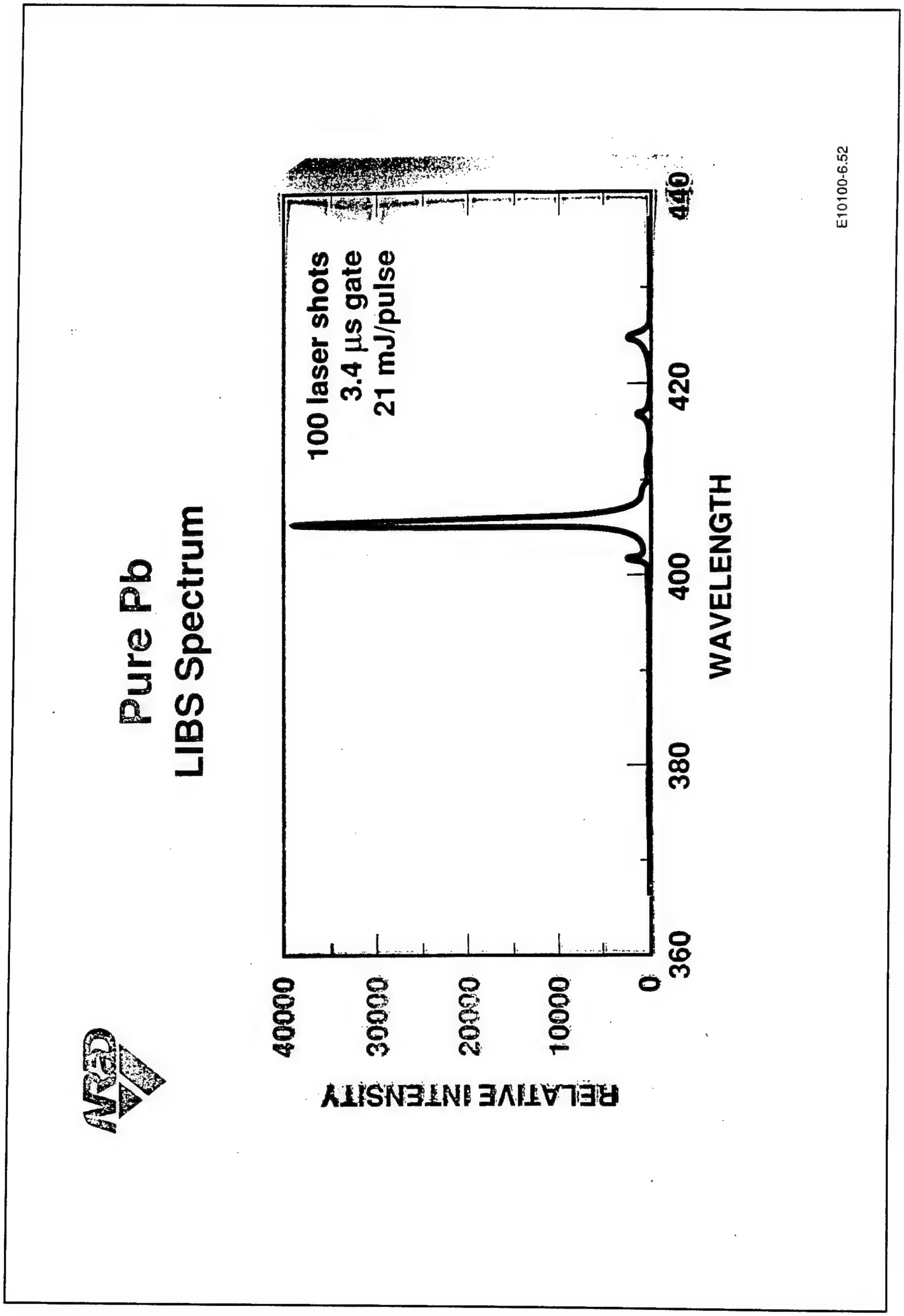
LIBS R&D TASKS

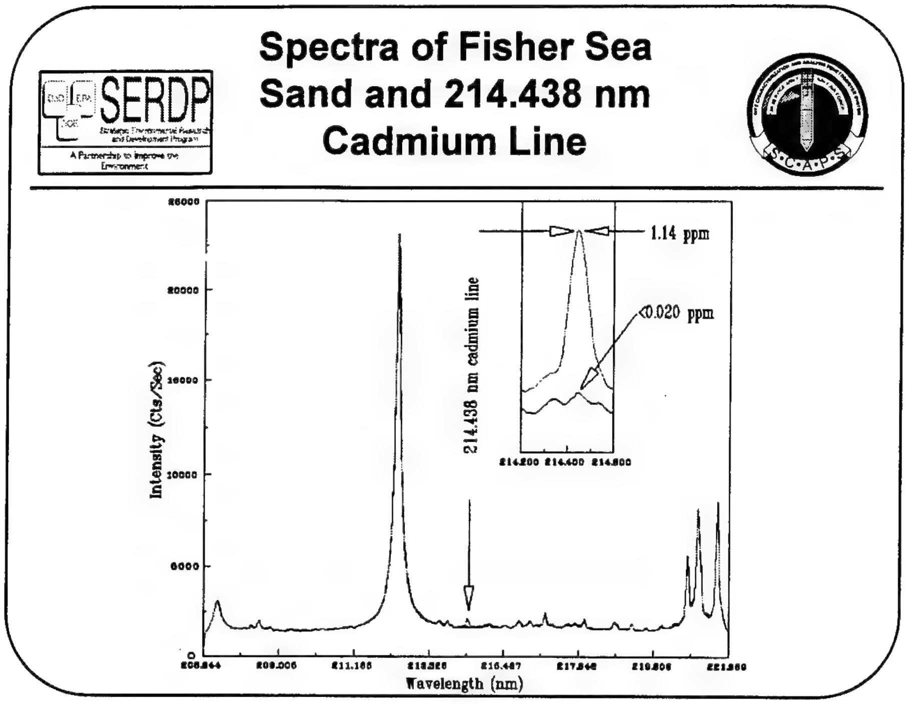
- **Evaluate approaches for in situ plasma generation**
  - WES - NRaD
  - LANL - UNL
- **Design & characterize fiber optic delivery system**
  - NRaD
- **Evaluate alternate detection methods**
  - ARL
- **Develop software techniques for automatic multi-element detection/quantification**
  - WES
  - NRaD
  - LANL

SCHEMATIC OF LIBS DIAGNOSTIC SYSTEM




Time Resolved LIBS
25 Laser shots
21 mJ/pulse
100 ns Gate
Pure Pb
150 µ spot
5 ns pulsewidth
RELATIVE INTENSITY
0
200
400
600
800
1000
1200
WAVELENGTH (nm)
360
370
380
390
400
410
420
430
440
TIME (ns)
0
1000
2000
3000


Pure Pb
LIBS Spectrum
100 laser shots
3.4 μs gate
21 mJ/pulse
RELATIVE INTENSITY
40000
30000
20000
10000
0
360
380
400
420
440
WAVELENGTH
E10100-6.52


Spectra of Fisher Sea
Sand and 214.438 nm
Cadmium Line
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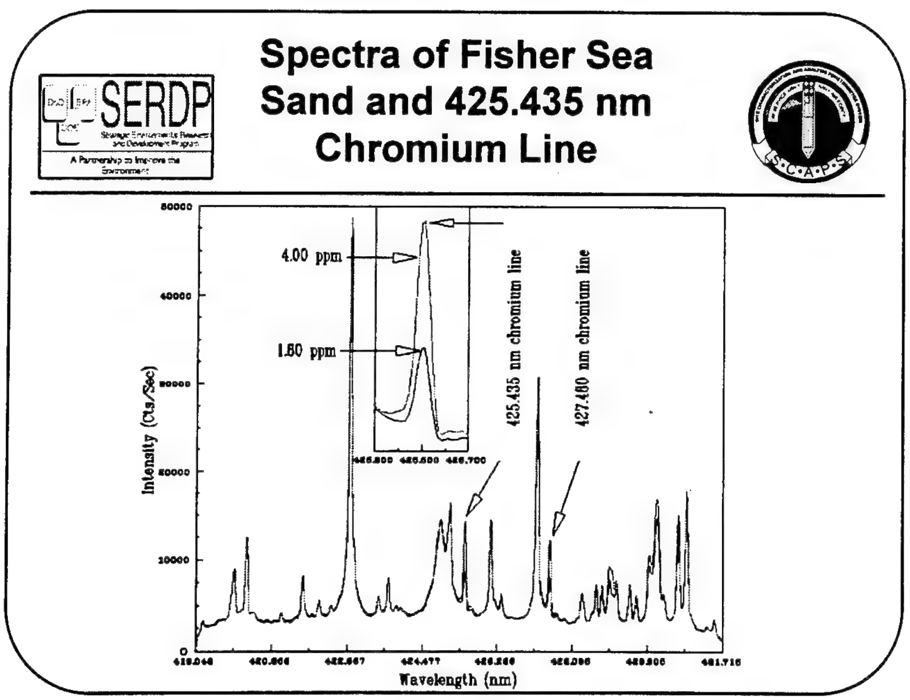
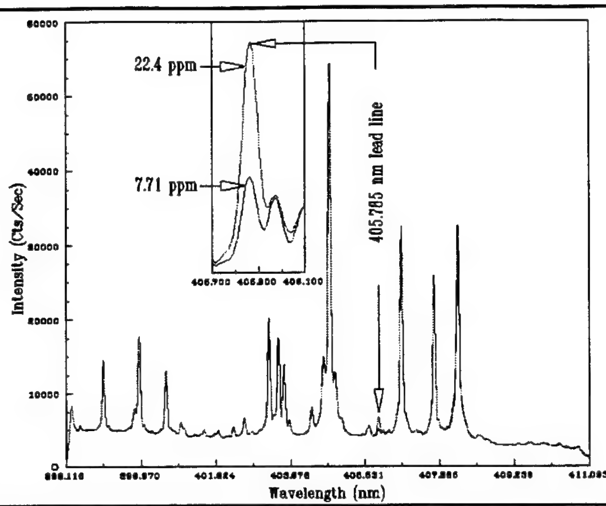
A Partnership to Improve the Environment
S•C•A•P•S
1.14 ppm
<0.020 ppm
214.438 nm cadmium line
Intensity (Cts/Sec)
Wavelength (nm)

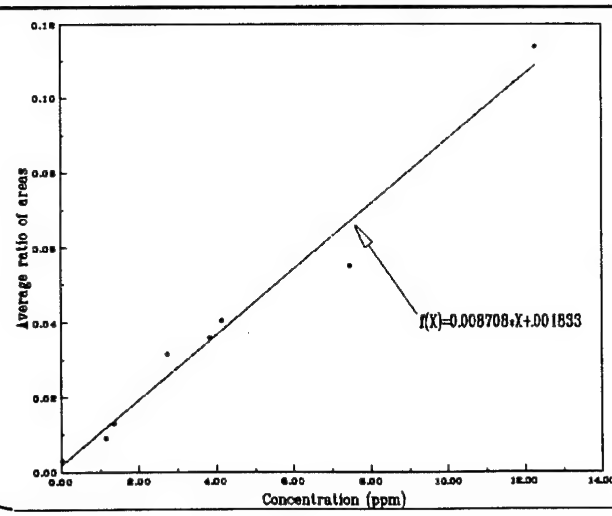

Spectra of Fisher Sea
Sand and 425.435 nm
Chromium Line
SERDP
A Partnership to Improve the Environment
S•C•A•P•S
4.00 ppm
1.80 ppm
425.435 nm chromium line
427.480 nm chromium line
Intensity (Cts/Sec)
Wavelength (nm)

Spectra of Yuma Sand and 405.785 nm Lead Line



Calibration Curve for Limit of Detection Limit Calculation

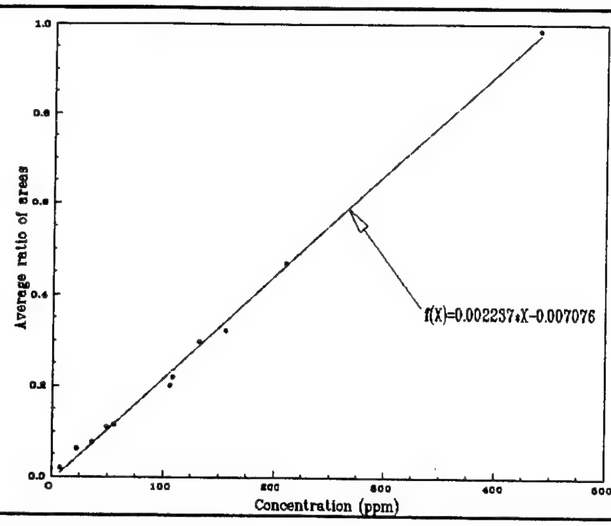
(Cadmium in Fisher Sea Sand at Laser Energy of 100 mJ)



LDL=0.56 ppm

Calibration Curve for Limit of Detection Calculation

(Lead in Yuma Sand at Laser Energy of 100 mJ)



LDL=9.14 ppm

LIBS Results Summary

Heavy Metal	Spectral Line nm	Background Concentration ppm	LIBS Lower Detection Limit ppm	EPA Action Levels Water ppm	EPA Action Levels Soil ppm
Pb	405.783	7.71	9.14	5.0	400.0*
Pb	405.783	1.53	3.32	5.0	400.0*
Cr	425.435	1.80	1.62	5.0	400.0**
Cd	214.438	<0.02	0.56	1.0	40.0
Hg	435.835	0.30	3.77	2.0	20.0
Zn	202.548	1.30	0.99	N/A	N/A

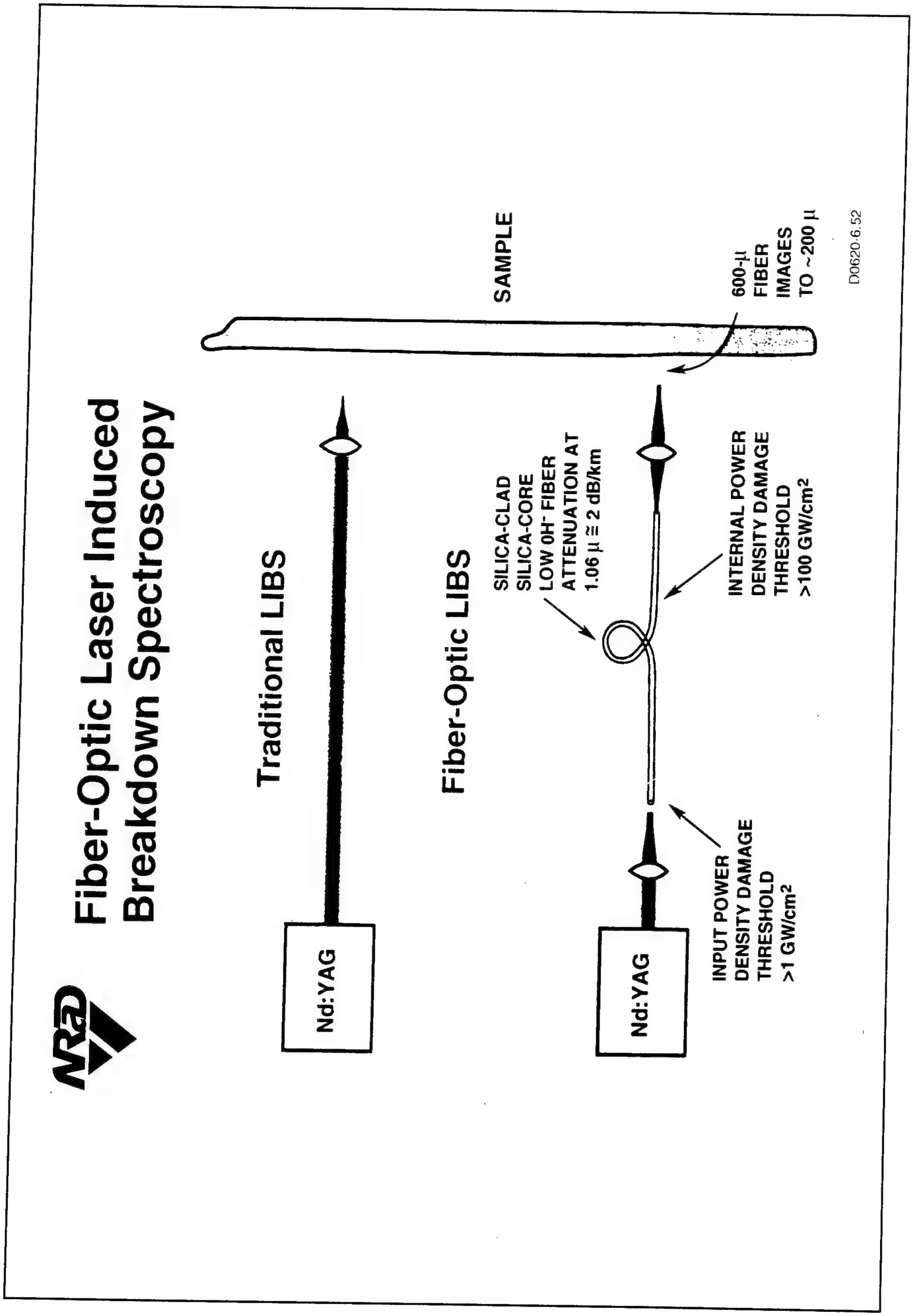
* Kentucky - Action level > background in soil (minimum 20 ppm)
Michigan - Action level 420 ppm in soil
Pennsylvania - Action level 200 ppm residential soil, and 600 ppm industrial soil
North Dakota - Action level 5 ppm in soil

** North Dakota - Action level 5 ppm in soil

Remote *in situ* detection of heavy metal contamination in soils using a fiber optic laser induced breakdown spectroscopy (FOLIBS) system

Gregory A. Theriault
Stephen H. Lieberman

Naval Command, Control and Ocean Surveillance Center
San Diego, CA


NRaD
Fiber-Optic Laser Induced Breakdown Spectroscopy
Traditional LIBS
Nd:YAG
SAMPLE
Fiber-Optic LIBS
Nd:YAG
INPUT POWER DENSITY DAMAGE THRESHOLD >1 GW/cm2
SILICA-CLAD SILICA-CORE LOW 0H- FIBER ATTENUATION AT 1.06 μ ≅ 2 dB/km
INTERNAL POWER DENSITY DAMAGE THRESHOLD >100 GW/cm2
600-μ FIBER IMAGES TO ~200 μ
D0620-6.52

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Desirable Features in a CPT Contaminant Probe

- Specific - Allows for Identification of Contaminant of Interest
- Simple - Requires Minimal Sample Preparation with only Optical Interrogation
- Rapid - Allows Site Characterization Decisions to be Made in Real Time
- Remote - Measurement to be Done Over Optical Fibers
- Inexpensive Probe

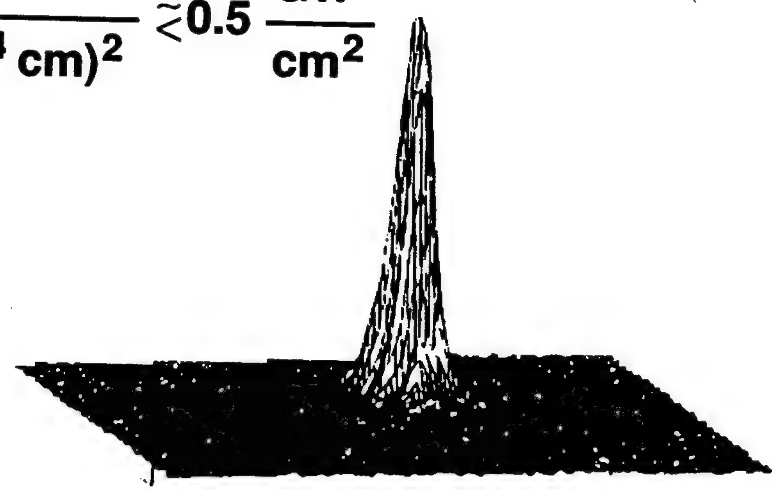
E0243-11.52

Spark Initiation Threshold on Soil

0.75 mJ, 9 ns Pulse, 150μ Spot

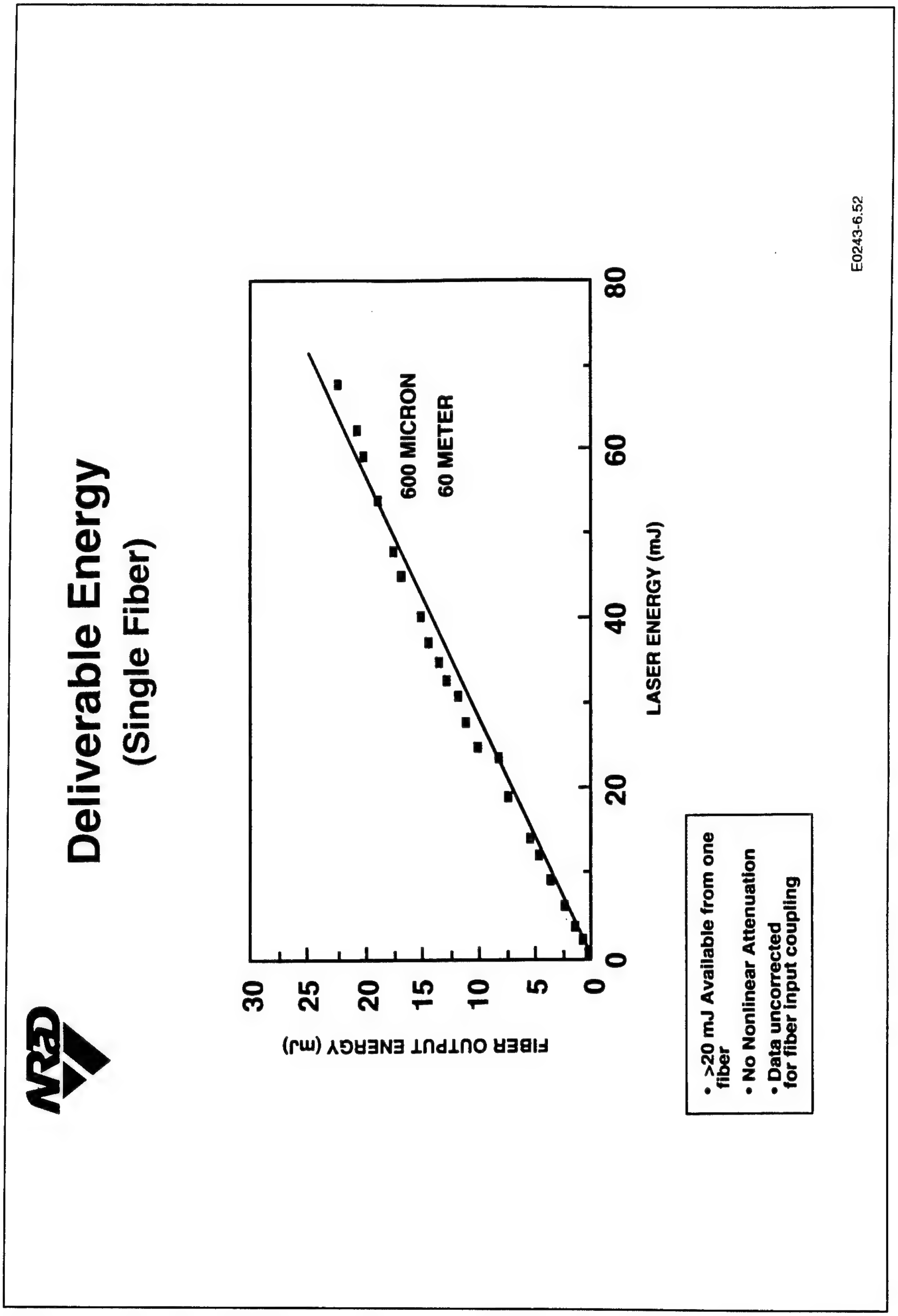
$$\frac{0.75 \times 10^{-3}\,\mathrm{J}}{9 \times 10^{-9}\,\mathrm{s}\,(\pi)\,(75 \times 10^{-4}\,\mathrm{cm})^2} \gtrsim 0.5\,\frac{\mathrm{GW}}{\mathrm{cm}^2}$$

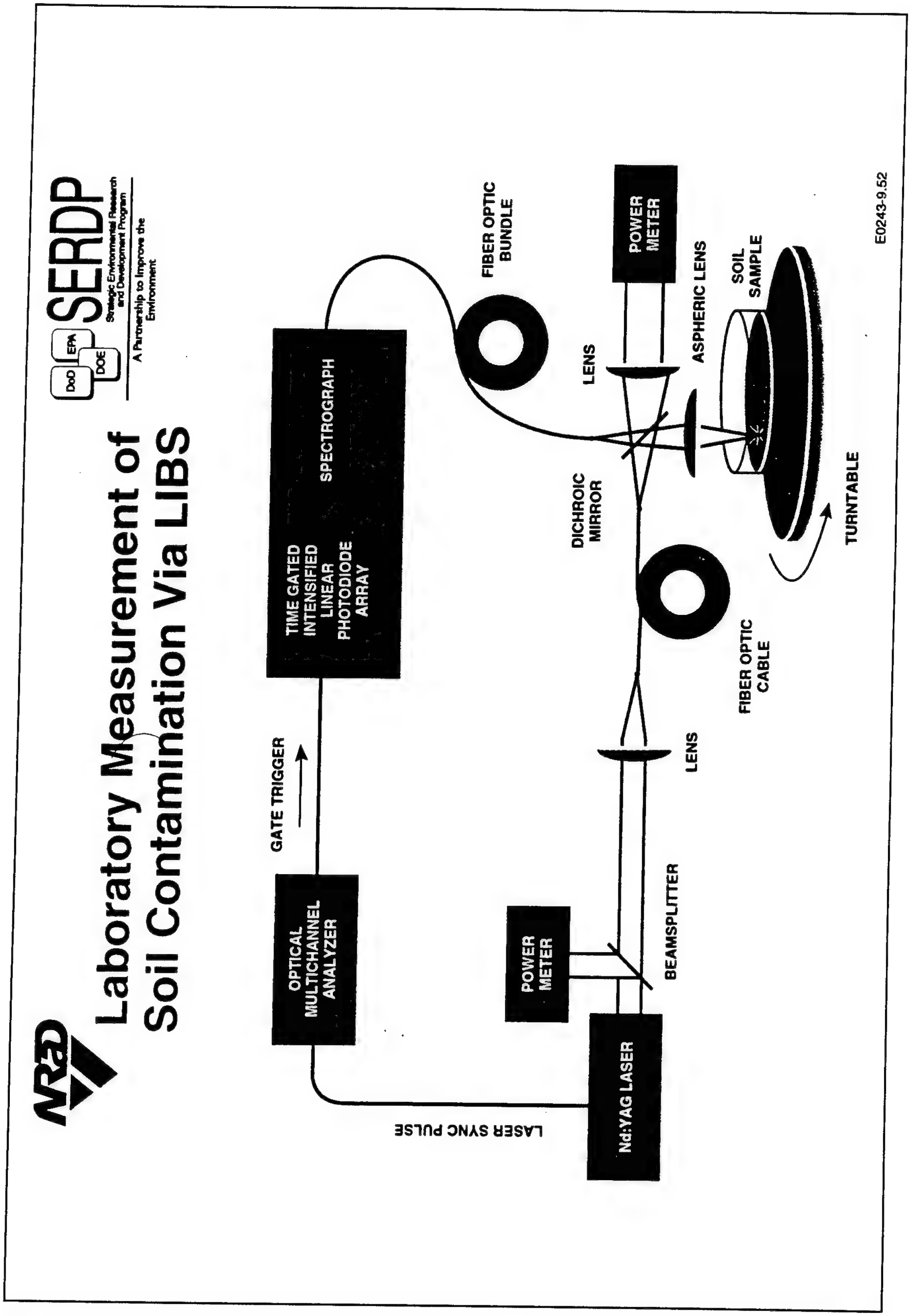
Soils Tested:
- Guadalupe
- Coronado I, II
- Yuma
- Alameda
- Camp Pendleton
- Fisher Sea Sand

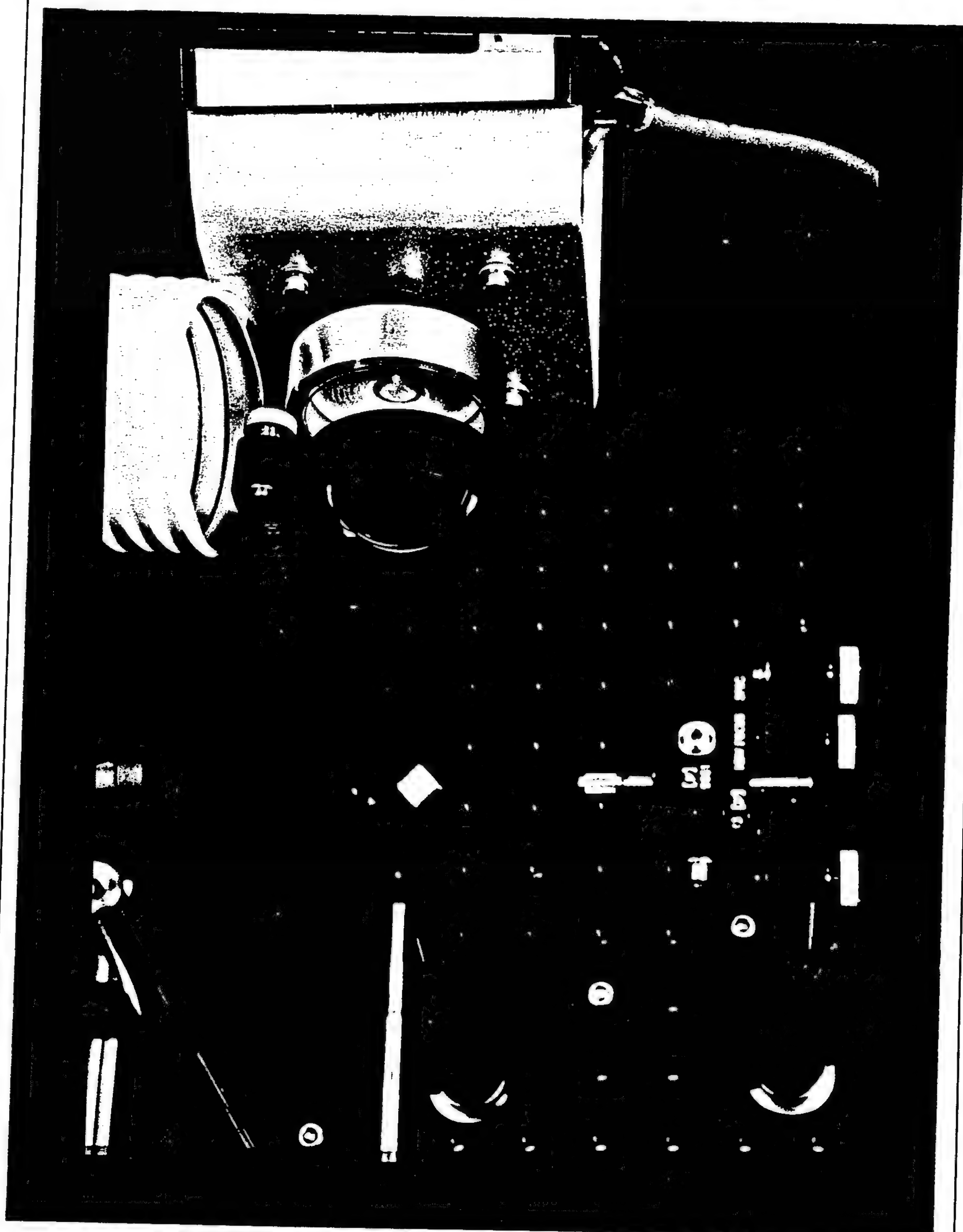


150μ DIAMETER SPOT SIZE

E10100-12.52


Deliverable Energy
(Single Fiber)
NR&D
600 MICRON
60 METER
FIBER OUTPUT ENERGY (mJ)
LASER ENERGY (mJ)
0
5
10
15
20
25
30
0
20
40
60
80
• >20 mJ Available from one fiber
• No Nonlinear Attenuation
• Data uncorrected for fiber input coupling
E0243-6.52


NRaD
Laboratory Measurement of
Soil Contamination Via LIBS
DoD
EPA
DOE
SERDP
Strategic Environmental Research and Development Program
A Partnership to Improve the Environment
OPTICAL MULTICHANNEL ANALYZER
GATE TRIGGER
TIME GATED INTENSIFIED LINEAR PHOTODIODE ARRAY
SPECTROGRAPH
FIBER OPTIC BUNDLE
POWER METER
LENS
ASPHERIC LENS
SOIL SAMPLE
DICHROIC MIRROR
TURNTABLE
FIBER OPTIC CABLE
LENS
BEAMSPLITTER
POWER METER
Nd:YAG LASER
LASER SYNC PULSE
E0243-9.52



Sample Spectra at Various Excitation Energies 100 ppm Lead on Sand

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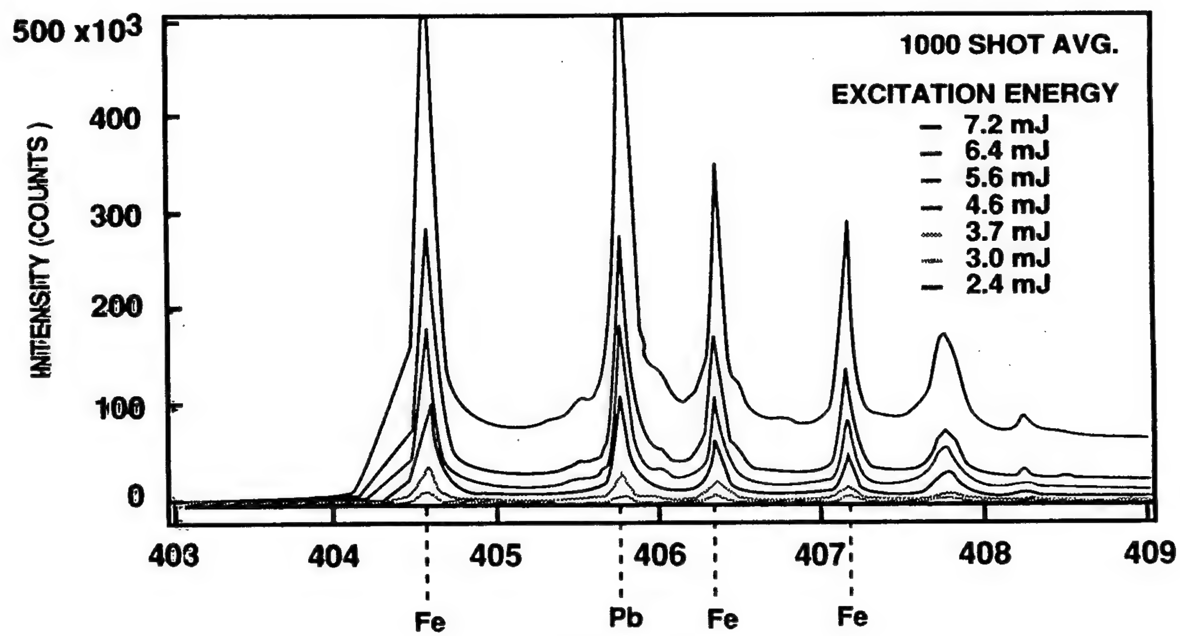
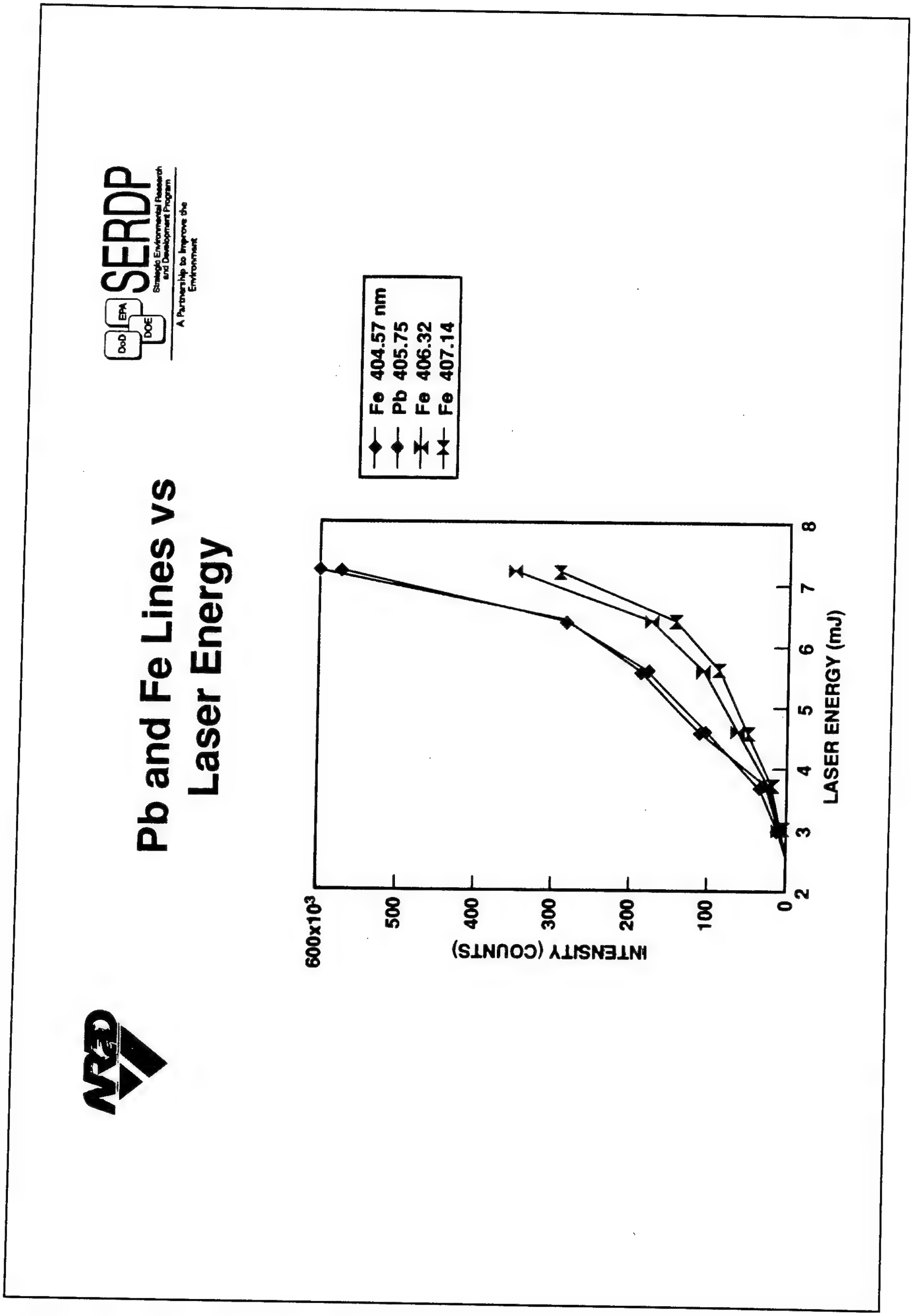


Fiber Optic LIBS


Pb and Fe Lines vs
Laser Energy
SERDP
Strategic Environmental Research and Development Program
A Partnership to Improve the Environment
DoD
EPA
DOE
INTENSITY (COUNTS)
600x10³
500
400
300
200
100
0
LASER ENERGY (mJ)
2
3
4
5
6
7
8
Fe 404.57 nm
Pb 405.75
Fe 406.32
Fe 407.14

SERDP
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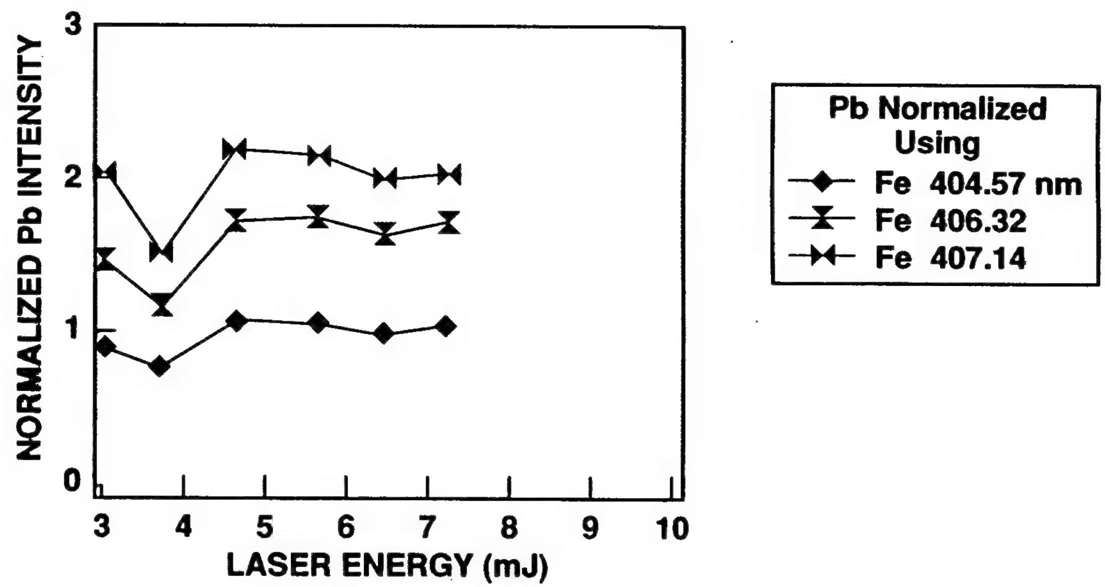
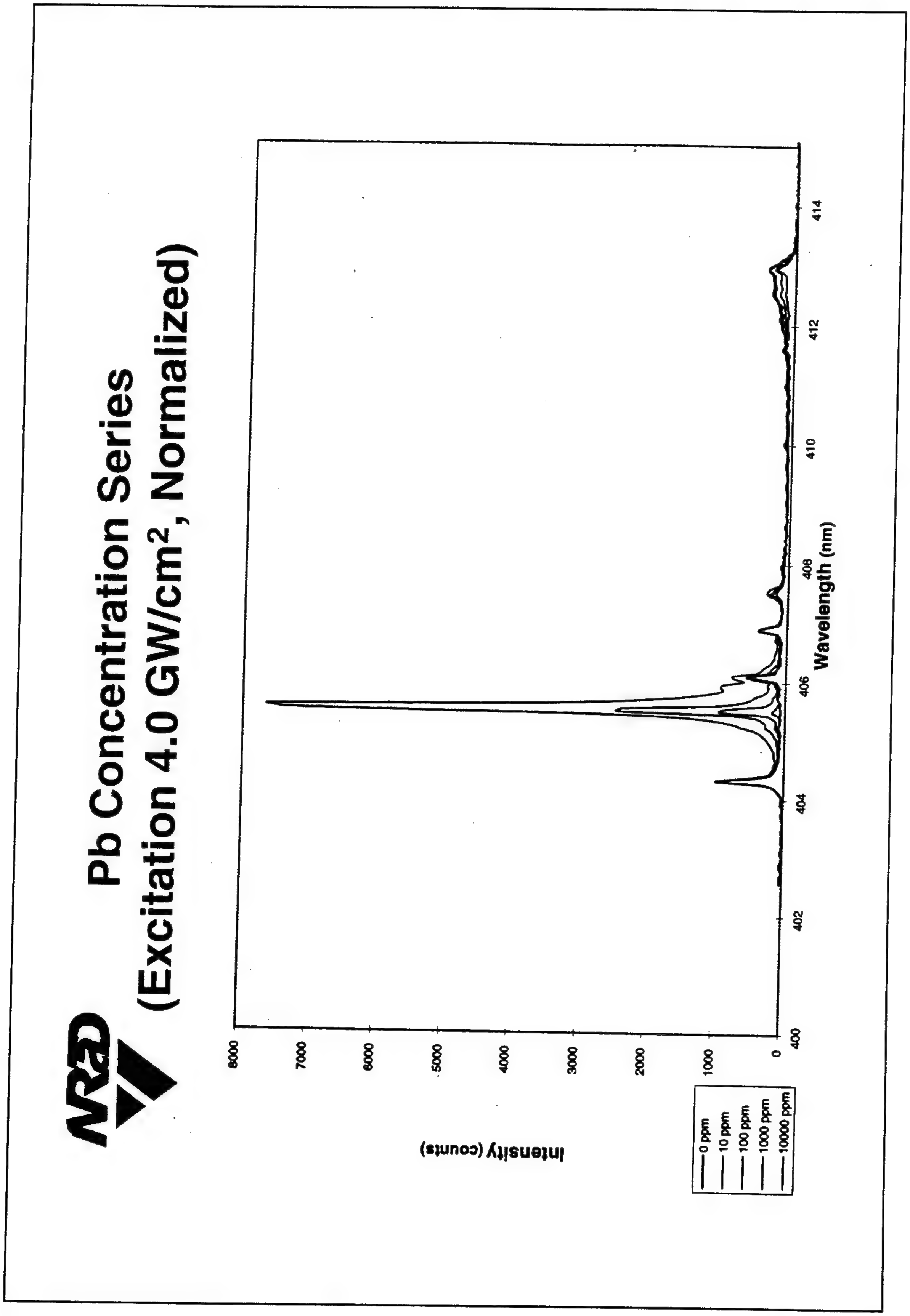
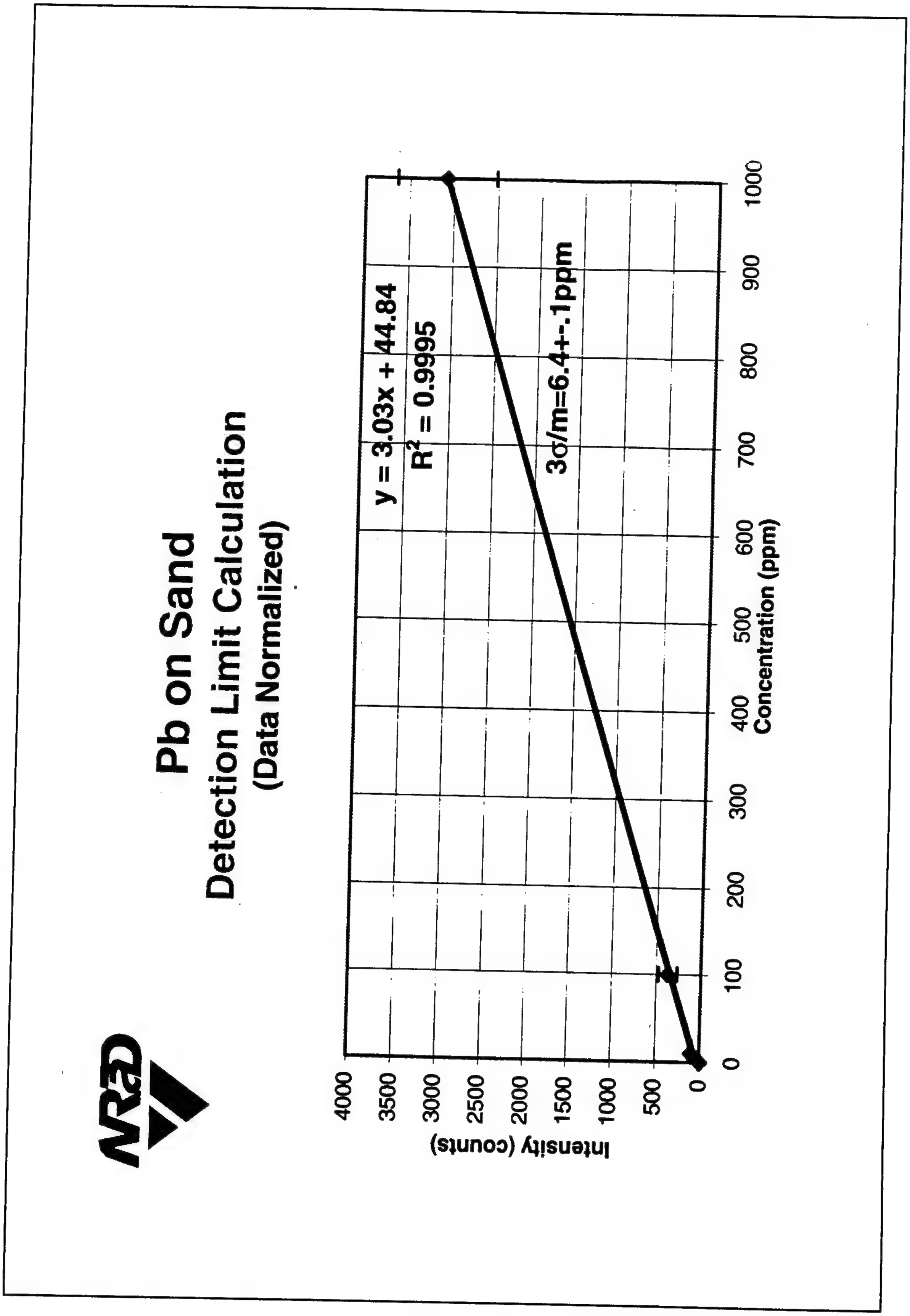
Pb/Fe Ratio vs Laser Energy

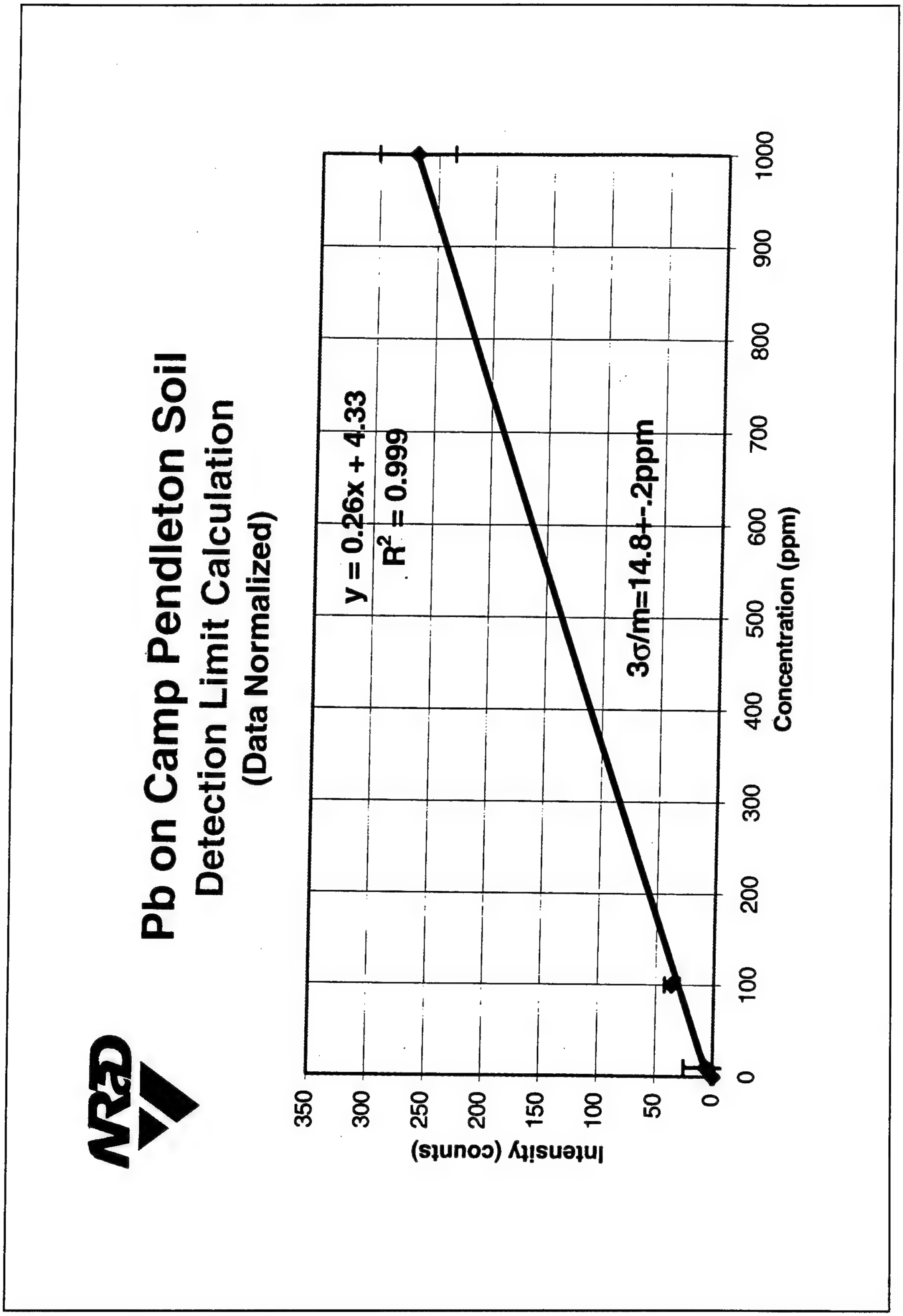


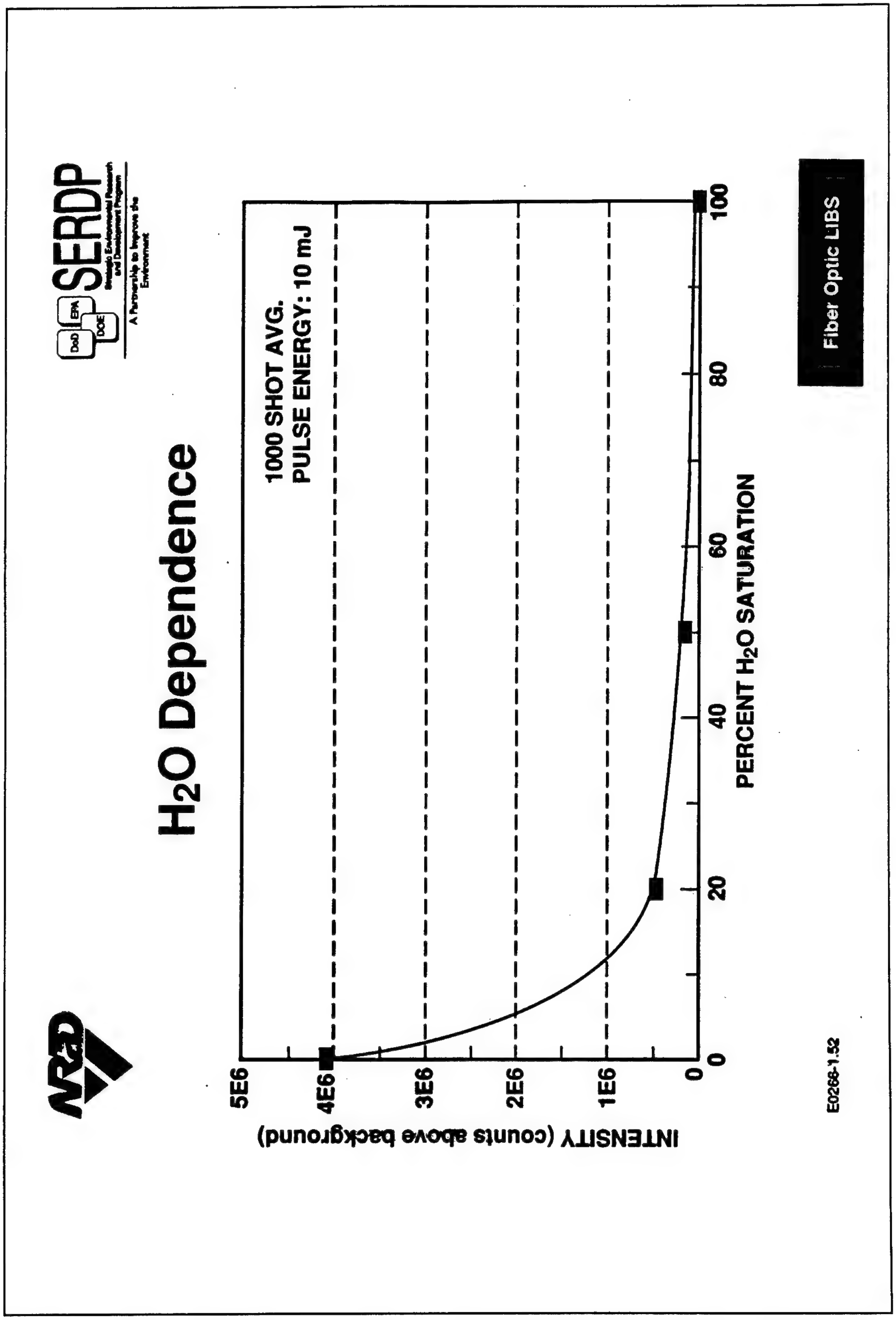
F0243-7.52

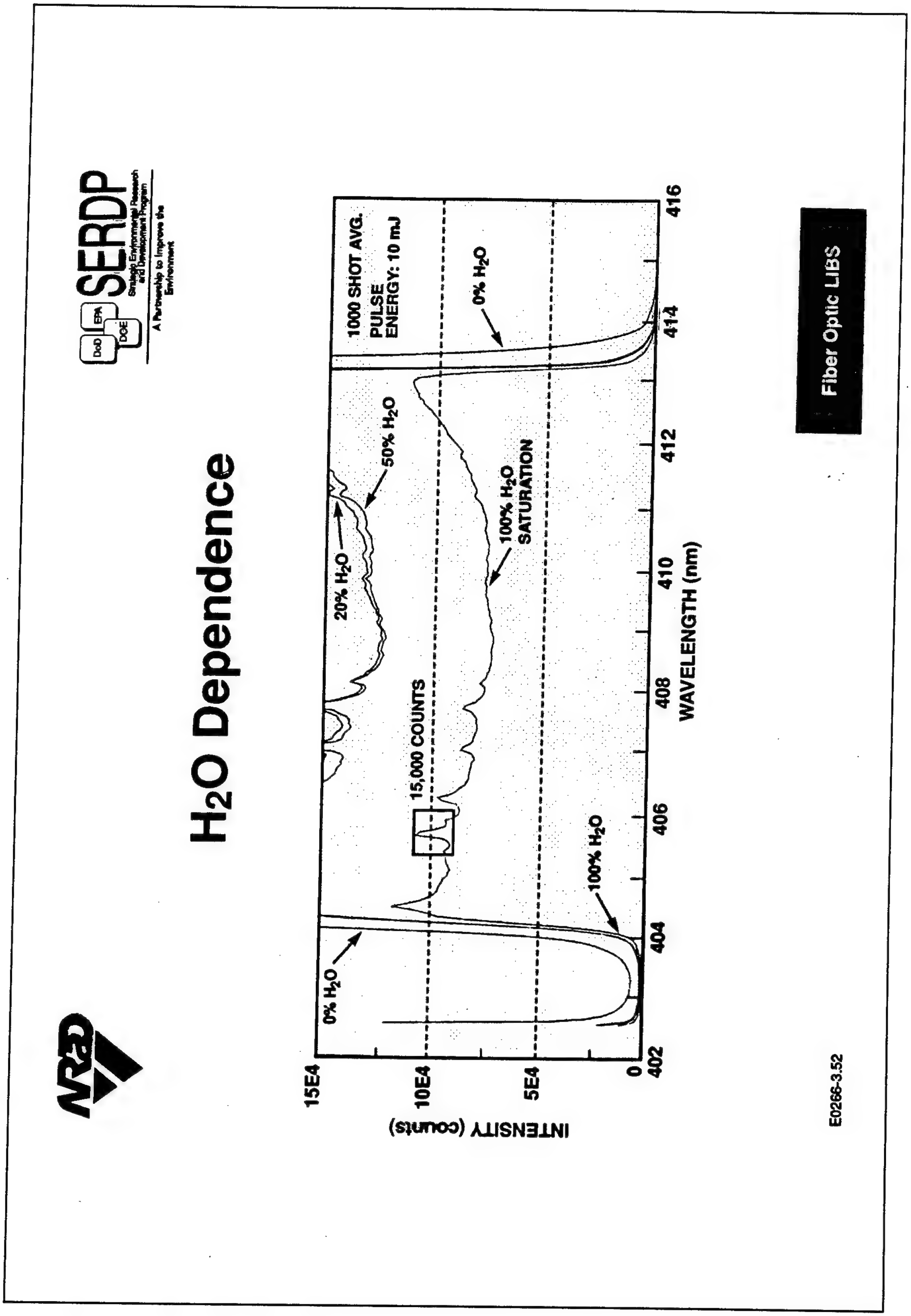


Pb Concentration Series
(Excitation 4.0 GW/cm2, Normalized)
Intensity (counts)
8000
7000
6000
5000
4000
3000
2000
1000
0
400
402
404
406
408
410
412
414
Wavelength (nm)
0 ppm
10 ppm
100 ppm
1000 ppm
10000 ppm


Pb on Sand
Detection Limit Calculation
(Data Normalized)
y = 3.03x + 44.84
R2 = 0.9995
3σ/m=6.4+-.1ppm
Intensity (counts)
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
4000
100
200
300
400
500
600
700
800
900
1000


NRaD
Pb on Camp Pendleton Soil
Detection Limit Calculation
(Data Normalized)
y = 0.26x + 4.33
R^2 = 0.999
3σ/m=14.8+-.2ppm
Intensity (counts)
0
50
100
150
200
250
300
350
Concentration (ppm)
0
100
200
300
400
500
600
700
800
900
1000


H2O Dependence
SERDP
DoD
EPA
DOE
A Partnership to Improve the Environment
1000 SHOT AVG.
PULSE ENERGY: 10 mJ
INTENSITY (counts above background)
5E6
4E6
3E6
2E6
1E6
0
0
20
40
60
80
100
PERCENT H2O SATURATION
Fiber Optic LIBS
E0266-1.52



H2O Dependence
DoD
EPA
DOE
SERDP
Strategic Environmental Research and Development Program
A Partnership to Improve the Environment
1000 SHOT AVG.
PULSE
ENERGY: 10 mJ
0% H2O
20% H2O
50% H2O
100% H2O
100% H2O
SATURATION
15,000 COUNTS
INTENSITY (counts)
15E4
10E4
5E4
0
402
404
406
408
410
412
414
416
WAVELENGTH (nm)
Fiber Optic LIBS
E0266-3.52

NRaD

Conclusions

- Detection capabilities on the order of ppm are possible with FOLIBS on sands and natural soils
- Matrix effects due to H_2O and finer grain size reduce sensor response
- FOLIBS is possible over long lengths of fiber
- The FOLIBS laser power delivery system is robust

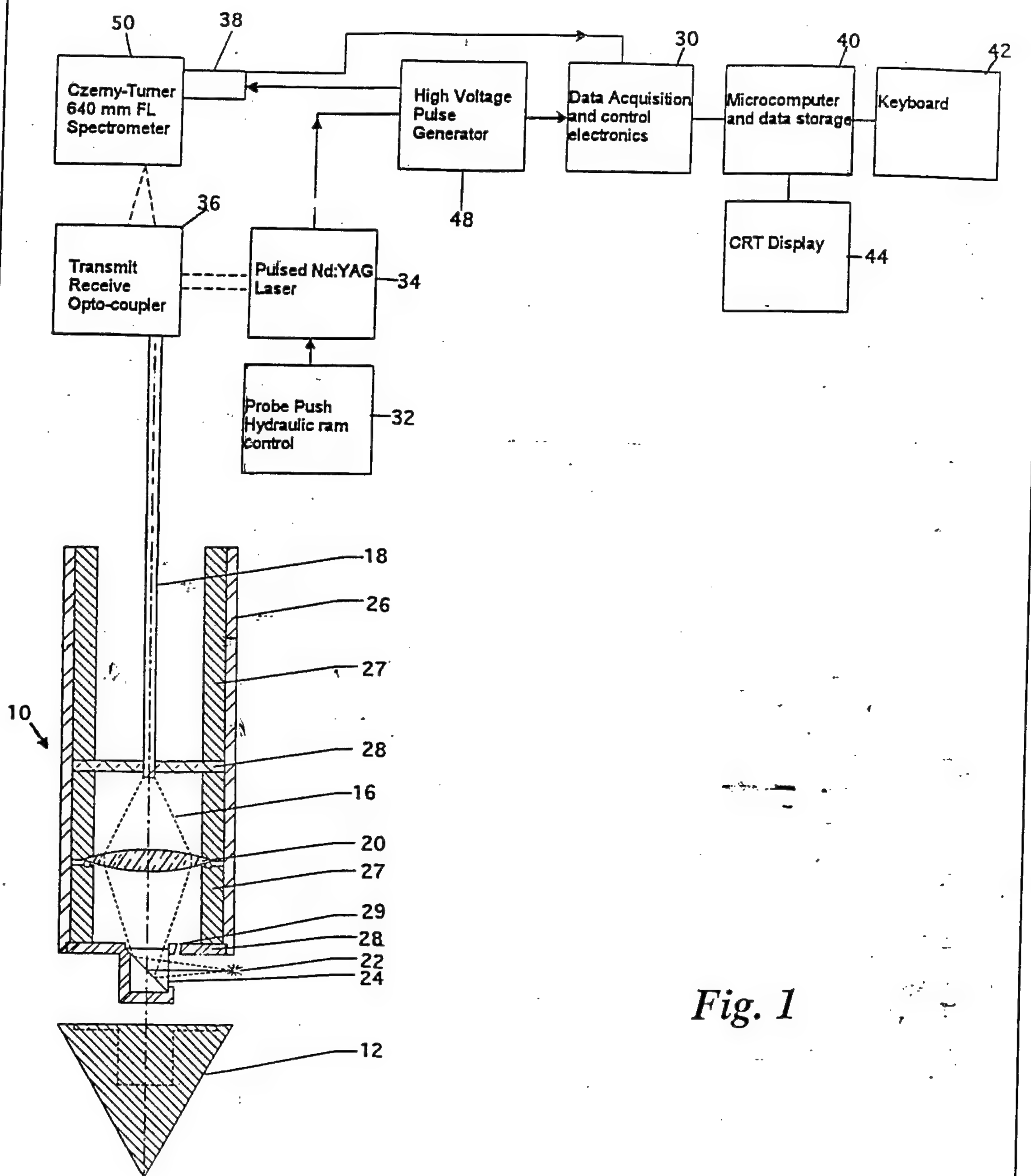
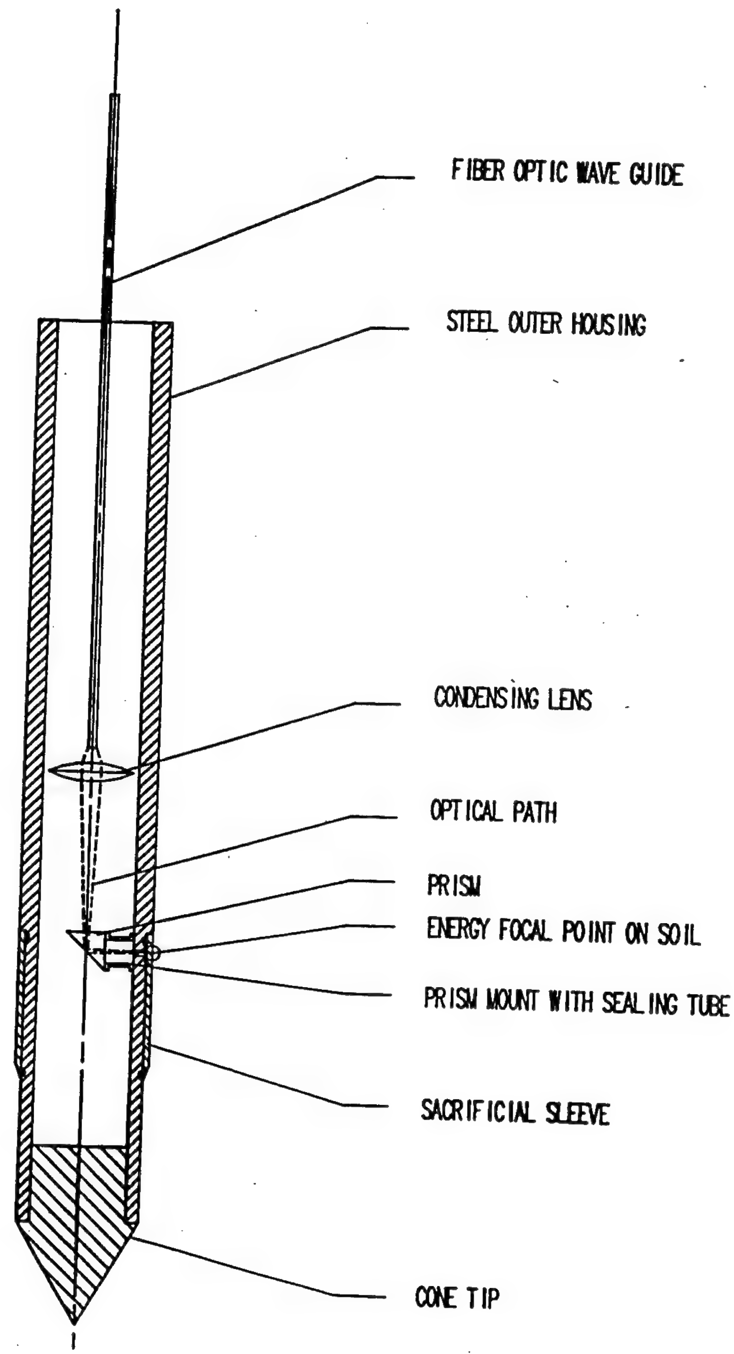

50
38
30
40
42
Czerny-Turner 640 mm FL Spectrometer
High Voltage Pulse Generator
Data Acquisition and control electronics
Microcomputer and data storage
Keyboard
48
36
Transmit Receive Opto-coupler
Pulsed Nd:YAG Laser
34
CRT Display
44
Probe Push Hydraulic ram control
32
18
26
27
10
28
16
20
27
29
28
22
24
12

Fig. 1


FIBER OPTIC WAVE GUIDE
STEEL OUTER HOUSING
CONDENSING LENS
OPTICAL PATH
PRISM
ENERGY FOCAL POINT ON SOIL
PRISM MOUNT WITH SEALING TUBE
SACRIFICIAL SLEEVE
CONE TIP

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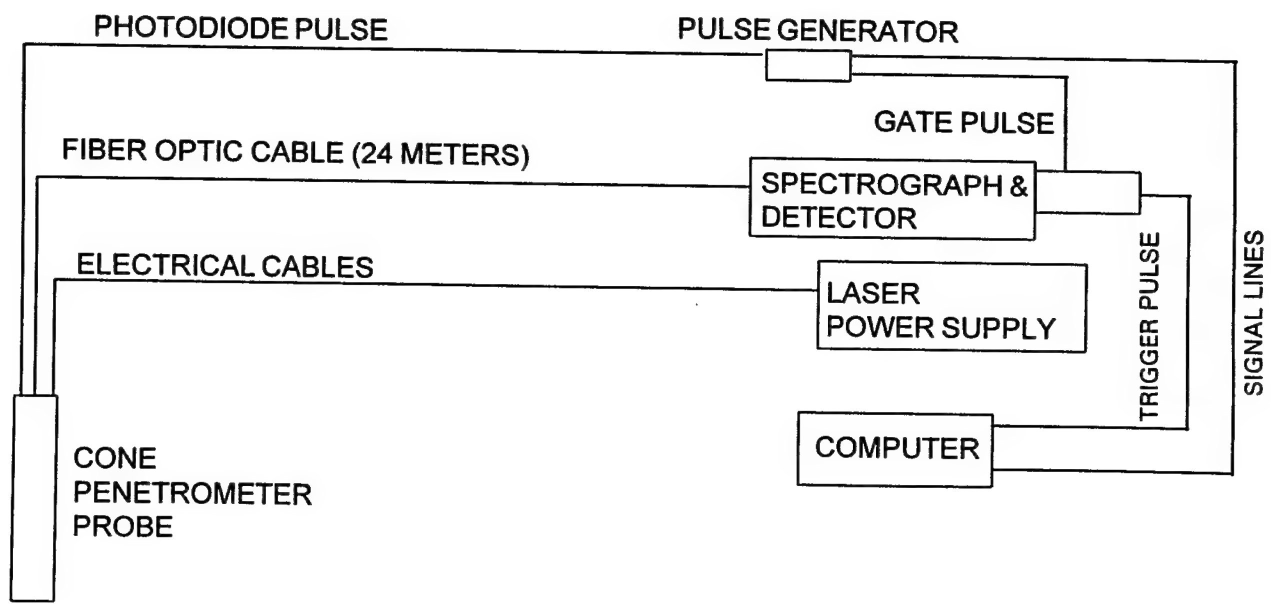
Strategic Environmental Research and Development Program
A Partnership to Improve the Environment

SCHEMATIC OF THE LIBS ANALYZER FOR SCAPS

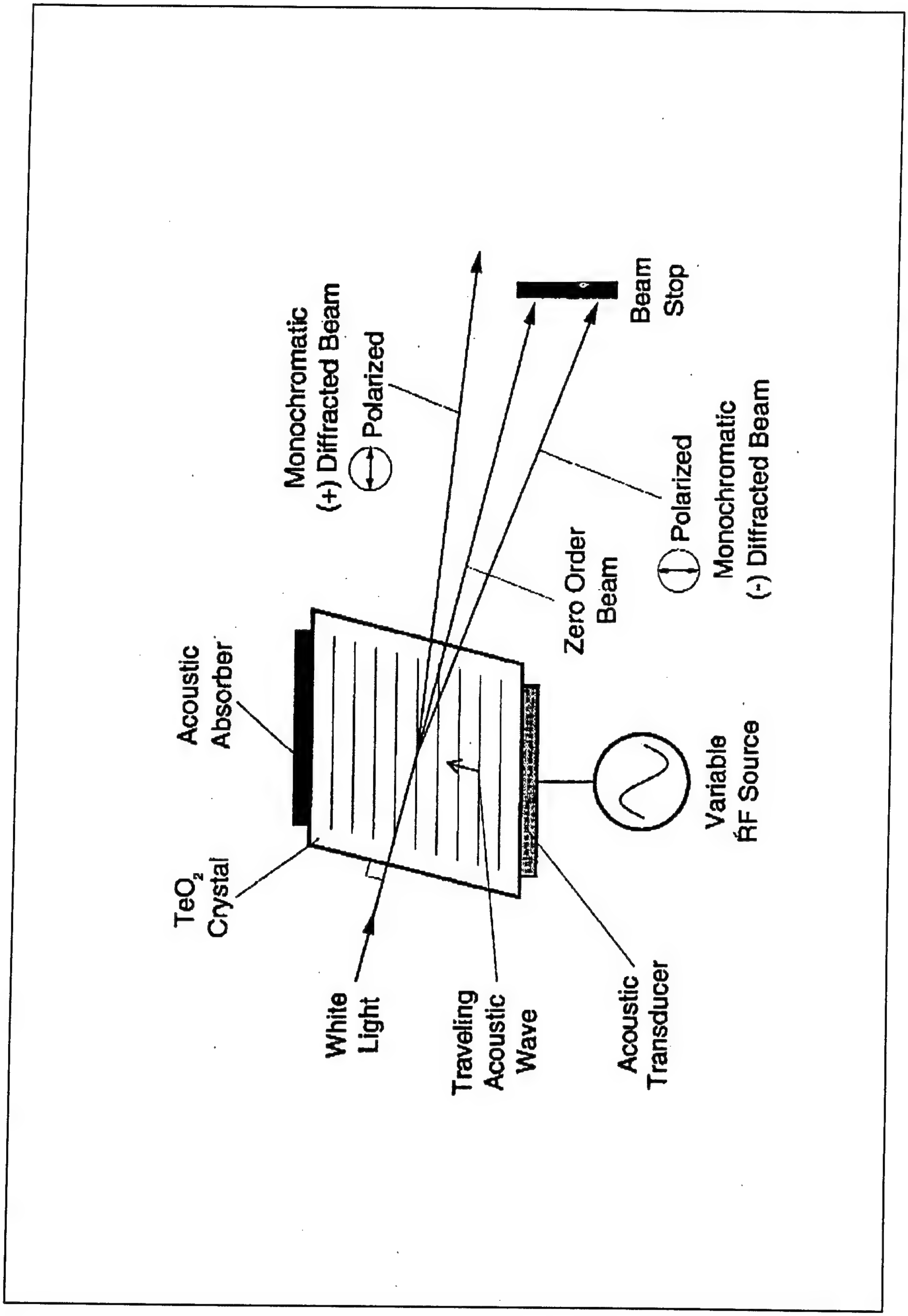


SYSTEM COMPONENTS

Laser	KIGRE Nd:YAG Osc/Amp system >80 mJ/pulse; 6 nsec pulsewidth; passively Q-switched; 1064 nm wavelength; 3-4 mm beam diam.; 1Hz rep. rate; passive air cooling; 24 meter cabling
Spectrograph	CHROMEX 250IS; 250 mm focal length; adjustable slits; 3600, 1200, and 600 l/mm gratings; all spectrograph functions are computer-controllable
Fiber Optics	Fused silica; 19 fiber bundle; circular-to-rectangular with CHROMEX mount; 24 meters long
Detector	ORIEL InstaSpec V; gated intensified CCD; 10nsec minimum pulsewidth gate; 10 Hz data acquisition rate; 25 mm CCD; 18 mm diam. intensifier; 650 pixels active
Gate/Trig Pulse Generator	Compact, LANL built
Computer	486 IBM Compatible
Software	SPECTRA © --LANL developed spectral analysis software

PRESENT STATUS OF PROJECT

- Software completed
- CHROMEX, fiber optics, and computer on hand
- Delivery of laser by 31 August 95
- Detector delivery by 11 September 95
  (use Insta Spec IV loaner in interim)
- System completed by 30 September 95


White Light
Traveling Acoustic Wave
Acoustic Transducer
TeO_2 Crystal
Acoustic Absorber
Variable RF Source
Zero Order Beam
Monochromatic (+) Diffracted Beam
Polarized
Beam Stop
Polarized
Monochromatic (-) Diffracted Beam

ACOUSTO OPTIC TUNABLE FILTER

Serial No.: 9506-AO-960

	SPECIFICATIONS	TEST DATA
Wavelength Range	380-600 nm	380-600 nm
Spectral Resolution (Å)	2 @ 380 nm 3 @ 600 nm	2 @ 380 nm 3 @ 600 nm
Corresponding Drive Frequency	200-350 MHz	218-434 MHz
Input/Output Polarization	Vertical	Vertical
Drive Power	1 Watt	1 Watt
Time Delay	10 μsec	10 μsec
Rise Time	30 μsec	30 μsec
Package Type	Air Cooled	Air Cooled
RF Connector	SMA	SMA

brimrose
5020 campbell blvd., baltimore, md 21236 usa • tel: 410/931-7200 • fax: 410/931-7206
e-mail: office@brimrose.com

New Quartz AOTF

- Wavelength Ranges:	200-400 nm
- Spectral Resolution:	1Λ @ 400 nm
	0.3Λ @ 400 nm
- Optical Aperture:	10 x 10 nm
- RF Frequency:	95-200 MHZ
- Driving Power:	8 Watts
- Input/Output Pol.:	Vertical/Horizontal]
- Diffraction Eff.:	> 50%
- Time Delay:	30 μs
- Rise Time	30 μs
- Package Type:	Air Cooled
- RF Connector:	SMA

PROGRESS

Yet to be Accomplished

- Compare quality of LIBS spectra between OMA and AOTF e.g. for Pb lines around 400 nm.

- Establish whether single-photon counting using AOTF on and off resonance at 10+ microseconds yields advantageous S/N ratios.

- Time-resolved studies of plasma evolution.

Characteristics

- Solid State Device, Compact (cm^3) and Ruggedize Moving Parts
- Fast Tuning Speed (several μs to tens of μs)
- Random Wavelength Access/Hopping
- NO "dead spectral space" for KHz Rate LIBS
- Simultaneously Multiple Wavelength Meassurement
- Spectral Imaging
- Built-in Solid State Chopper for Lock-in Amplification

PROGRESS

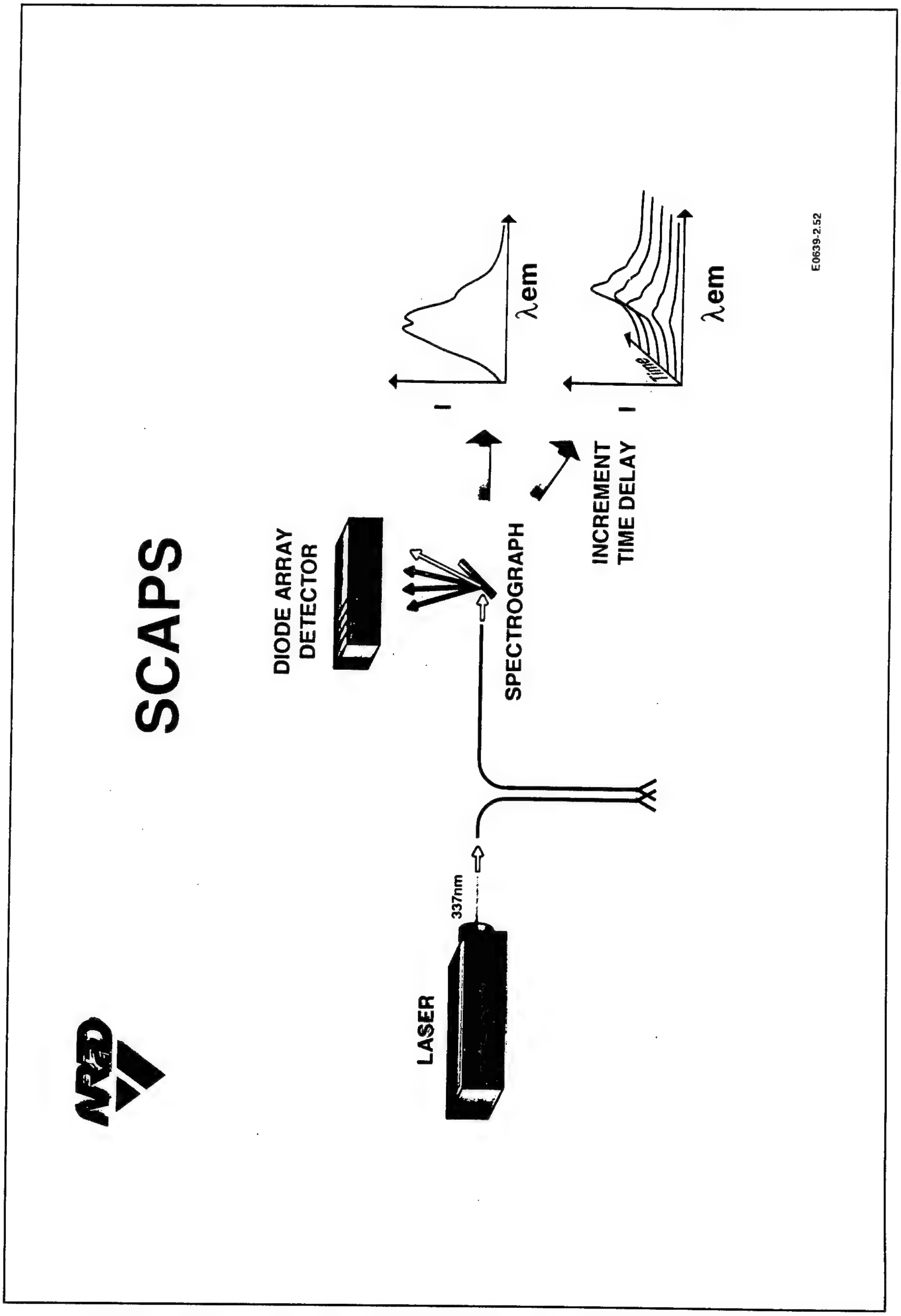
Equipment Acquired

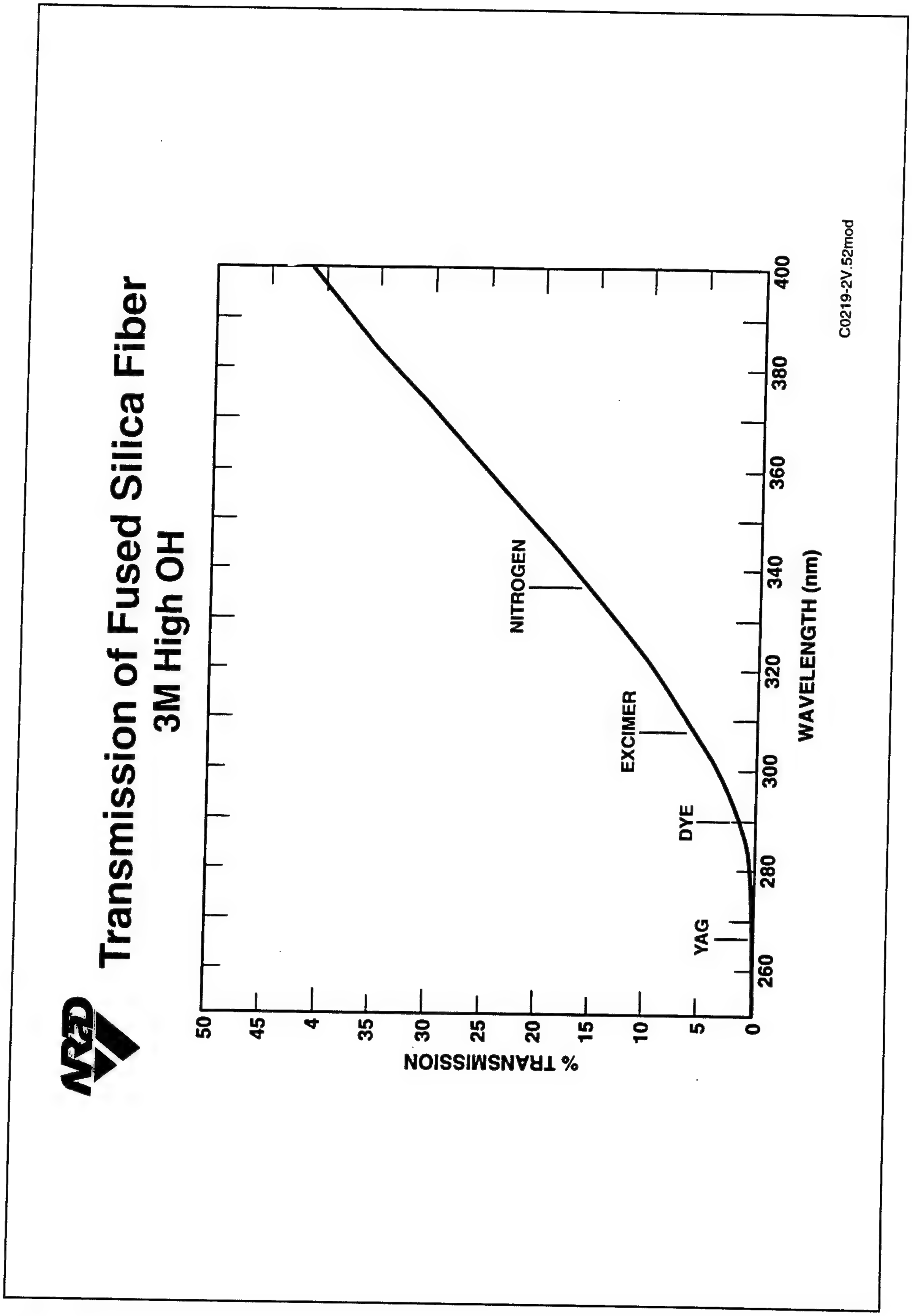
- "Ultra-High Resolution" AOTF, State-of-the-Art commercial unit Spectral resolution ca. 0.3 nm
- Compact and portable Nd:YAG Laser (Big Sky Laser Model CFR 200-20 with mini CE portable power supply)
- 4-channel digital scope (LeCroy Model 9354TM-500MHz) with 500 Ms/s and 500K point record length/channel.

RESEARCH AREA II
LIF SENSOR

Milestones

	Schd	Reschd	Comp
• LIF POL Sensor			
– Complete development of improved POL sensor	03/95		03/95
– Complete field demonstrations of improved POL sensor	03/96		
• Photofragmentation/LIF Explosives Sensor			
– Demonstrate feasibility of PF/LIF for in situ explosives sensor	09/95		
– Complete prototype sensor	09/96		
– Complete field tests of explosives sensor	12/96	06/97	


SCAPS
LASER
337nm
DIODE ARRAY
DETECTOR
SPECTROGRAPH
INCREMENT
TIME DELAY
I
λem
Time
E0639-2.52


Transmission of Fused Silica Fiber
3M High OH
% TRANSMISSION
50
45
4
35
30
25
20
15
10
5
0
260
280
300
320
340
360
380
400
WAVELENGTH (nm)
YAG
DYE
EXCIMER
NITROGEN
C0219-2V.52mod

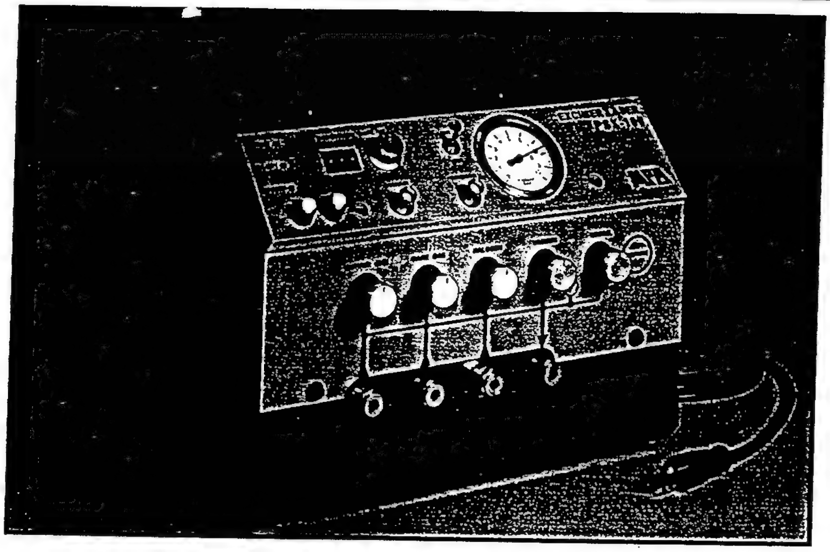
XeCl Excimer Laser

- wavelength: 308 nm
- pulse energy: 2 mJ
- repetition rate: 100 Hz
- Gas: 99.7% He
  0.07% HCl
  0.2% Xe
- Laser pulses per fill: 3,000,000
  (8 hours or roughly 16 pushes)
- Fills per bottle of gas: ~100

MPB TECHNOLOGIES INC.

Cryogenic Rare gases

PSX-100 Excimer Laser



The Model PSX-100 is an innovative multi-gas excimer laser which is both compact and portable and yet is capable of mJ pulse energies and, with a pulse duration of only 2.5 ns, peak powers in excess of 2 MW.

Both the laserhead and the power supply are incorporated in a single unit less than 1 ft. in length. The laser operates in a sealed-off mode and, despite its small gas volume, exhibits very respectable gas fill lifetimes even without the use of a gas processor.

The PSX-100 has been carefully engineered throughout, from its high-efficiency discharge circuit (with negligible reverse aftercurrent) to the use of high-quality, durable discharge circuit components and the careful selection of halogen compatible materials for the gas and discharge chamber.

Given its pulse energy and peak power capabilities, the PSX-100 represents a convenient and cost effective alternative to larger, much more costly lasers for many photoablation and micromachining applications. In addition, the laser's 2.5 ns pulse duration, unique among available excimer lasers, offers new possibilities in areas such as relaxation time studies and time resolved spectroscopy.

With its sealed-off mode of operation, air cooling and low power budget (100 W), the PSX-100 is also ideally suited for field use outside the laboratory.

Features

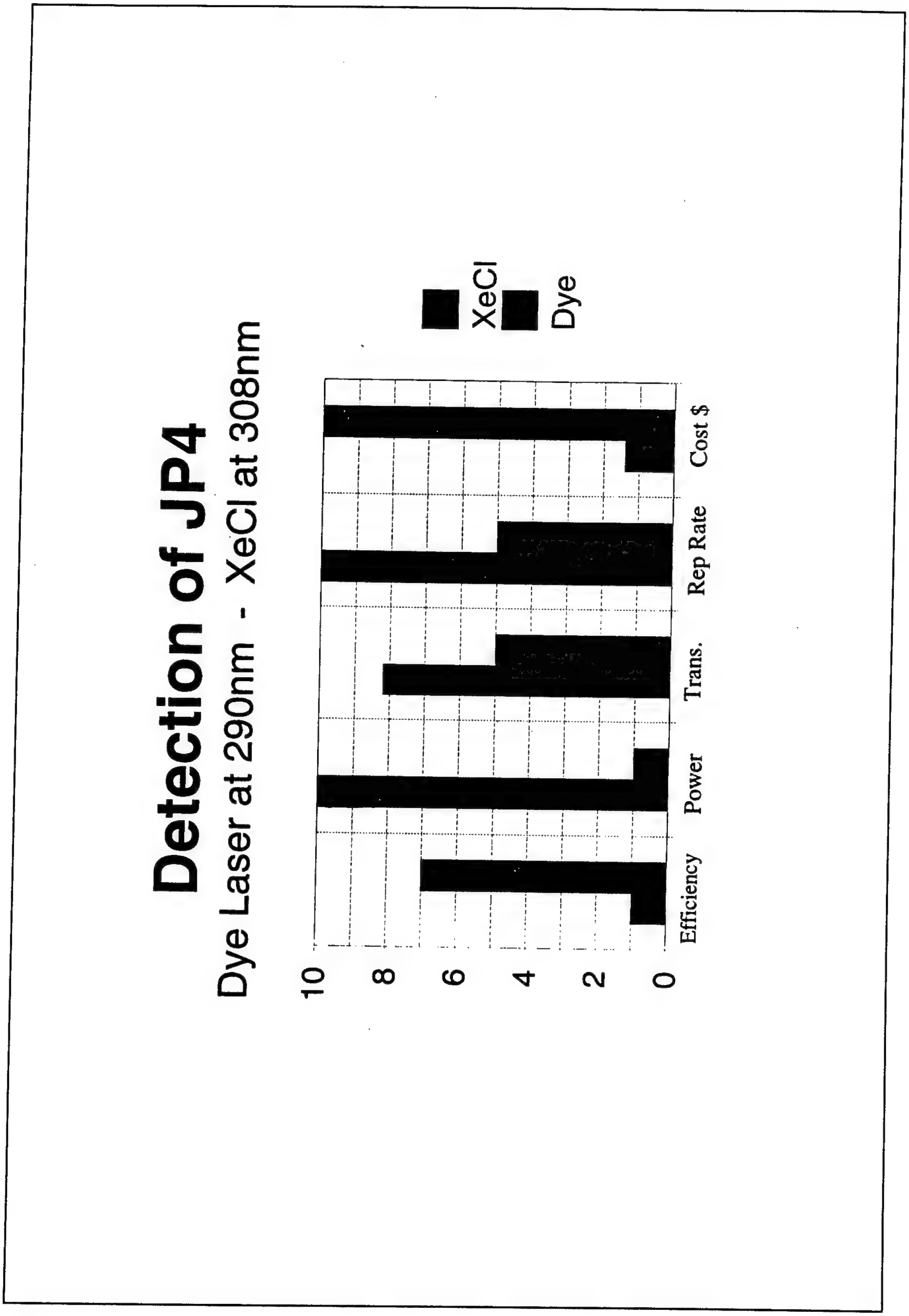
- Compact single unit construction
- Air cooled
- Short, high peak power pulses
- Efficient discharge circuit with negligible reverse aftercurrent
- Long thyratron life (> 3 x 10^8 pulses)
- Halogen compatible construction for minimal repassivation
- Multi-gas optics (optional)
- Automatic gas refill (optional)

Applications

- Photoablation and micromachining
- Semiconductor processing
- Surface analysis
- Laser ionization mass spectroscopy
- Fluorescence spectroscopy
- Photochemistry
- Relaxation time studies
- Nonlinear optics

SCAPS using Excimer laser

- **Advantages**
  - Nitrogen laser can be directly replaced by excimer laser without changes to detection system/software
  - Less gas required compared to Nitrogen system
- **Disadvantages**
  - Added complexity working with toxic gases (small amount of HCl in excimer gas)


Detection of JP4
Dye Laser at 290nm - XeCl at 308nm
10
8
6
4
2
0
Efficiency
Power
Trans.
Rep Rate
Cost $
XeCl
Dye

Excimer Laser Results

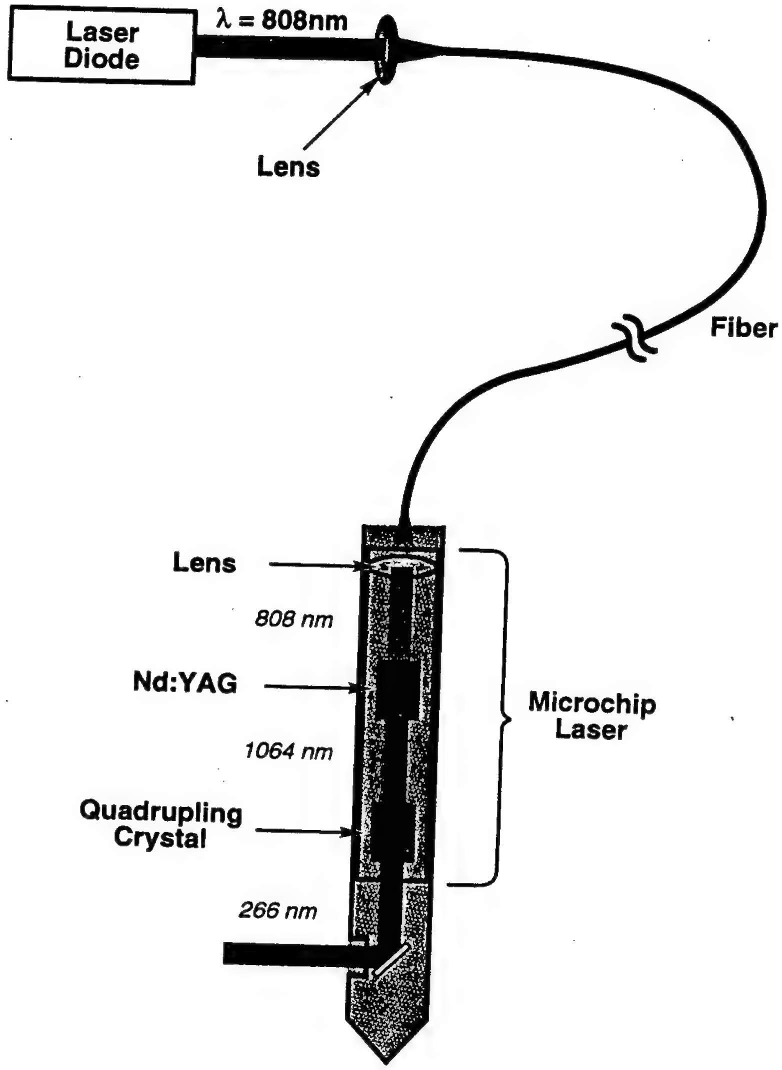
- integration into present SCAPS hardware straightforward

- laser very sensitive to gas contamination
  - operation ≤ 30 min per fill at present

Timetable for fielding

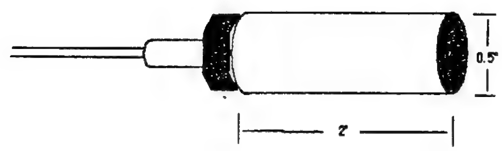
- lab evaluation: Underway
- field testing: First Quarter FY 96

Schematic of Downhole 266 nm Wavelength Microchip Laser



A0147-1.52mod

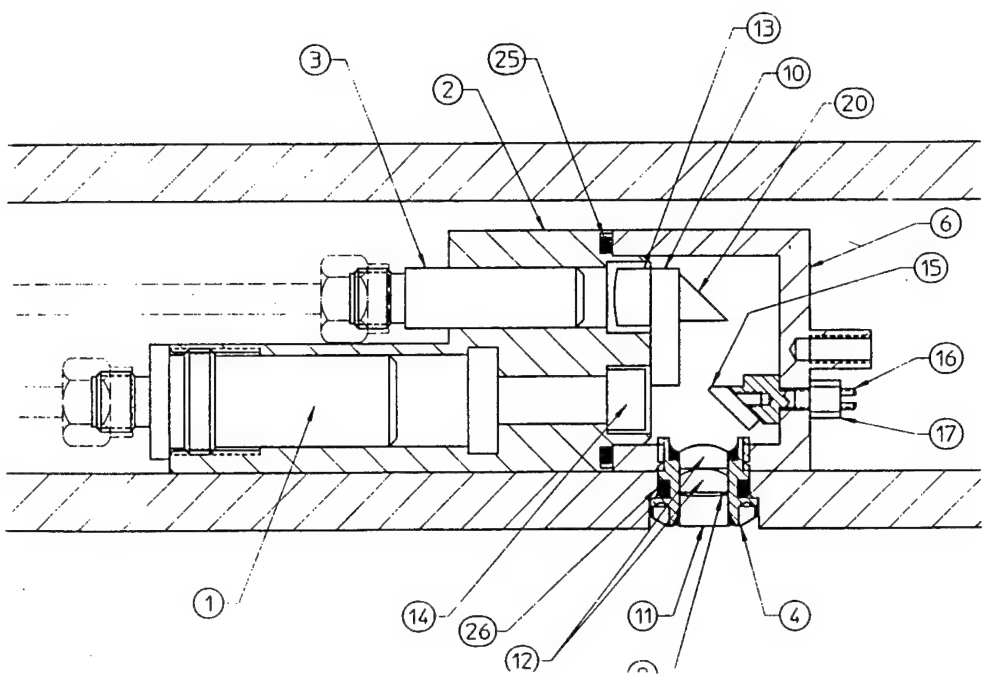
Microchip Laser



- **wavelength:** **266 nm**
- **power:** **5 mW**
- **pump source:** **1.2 W laser diode (located in truck)**
- **lifetime:** **100,000 hours**
- **material:** **Nd:YAG (all soild state; no gas required)**
- **source:** **M.I.T. Lincoln Labs**

Prototype Microchip Laser Probe

- **Laser & collection fiber:**



Microchip Laser Collaboration

- **Partners:** NRaD, San Diego
  MIT Lincoln Labs, Concord MA

- **Lincoln Lab tasks**
  - originally developed microchip laser (1064 nm)
  - frequency quadrupled output (266 nm)
  - frequency tripled output (355 nm)
  - designed mount for use in penetrometer

- **NRaD tasks**
  - integrate microchip laser into SCAPS
  - laboratory evaluation of LIF using 266 nm
  - field testing of SCAPS/microchip laser system

- **Timetable**
  - lab evaluation: Underway
  - field testing: Second Quarter FY 96

NRaD

Lasers for LIF Sensor

Laser	Wavelength (nm)	Cost ($K)
nitrogen	337	8
XeCl	308	12
Tuneable (ROST)	290 (variable)	100
Lipstick Nd:YAG	266	8

DoD EPA DOE

SERDP

Strategic Environmental Research and Development Program

A Partnership to Improve the Environment

Accelerated Tri-Services SCAPS Sensor Development

Laser Induced Fluorescence and Fiber Optic Raman Sensors

ARMSTRONG LABORATORY

Mr. Bruce J. Nielsen
Environics Directorate
Site Remediation Division

Laser Induced Fluorescence (LIF) and Fiber Optic Raman Sensors (FORS)

Objective: Perform Fluorescence and Raman Sensor R&D for SCAPS, Based on Tunable (ROST) Technology.

Approach:

- **Provide for Refinement of Prototype Systems**
- **Test in Lab & Field Environments**
- **Determine Device Applicability**

Payoff:

- **Applicable to Site Characterization and Monitoring**
- **Accurate and Reliable Results**
- **In Situ, Real-Time Data**
- **Reduced Characterization and Monitoring Costs**
- **Remediation Process Control**

Laser Induced Fluorescence Sensors

LIF POL Sensor

Principal Investigator: Dr Greg Gillispie
Dakota Technologies, Inc./North Dakota State University

Emphasizes Use of Tunable Dye Laser

- **Study Soil Matrix Effects on Fluorescent Properties of Aromatic Hydrocarbons**
- **Oxygenated Versus Deoxygenanted Matrices**
- **Laboratory Testing Indicates Detection of #2 Diesel, DFM, Unleaded Gasoline, and JP-4 on Sand, Soil From China Lake, and Soil From Columbus AFB at 100 ppm or Lower Concentrations.**

Laser Induced Fluorescence Sensors (cont.)

Research Questions:

- **How Much Chemical Information Can Be Derived From Fluorescence Spectra?**
- **What Are the Detection Limits?**
- **How Linear Is the Calibration Curve?**
- **Deviations at Low and High Concentration Ends?**
- **Can Dissolved Phase Aromatic Hydrocarbons Be Detected?**

Laser Induced Fluorescence Sensors (cont.)

Results:

- **Developed Apparatus/Method for Spiking Soil Samples**
  - **Teflon Containers/Paint Can Shaker**
  - **Nonstick Surfaces/Good Mixing**
- **Five Soil Types Spiked With Diesel Fuel**
  - **Sand Fluorescence Response 10X Silty Matrix**
  - **Sand Fluorescence Response 100X Peat or Lean Clay Matrix**
- **Will Collaborate with WES Matrix Study**
  - **Ten or More Soils**
  - **Four Common Fuels**
    - **Gasoline, Jet Fuel, Diesel #2, DFM**

Laser Induced Fluorescence Sensors (cont.)

Tasks

(1) Pattern Recognition Techniques
- **Chemometrics (MATLAB Code to Analyze WTM Data)**
- **Time Resolved Excitation Emission Matrices (TREEMs)**

(2) Lower Detection Limits by Better Probe Design
- **The Probe Design Will Be Carefully Reassessed to Better Reject the Scattered Exciting Light, Especially With Regards to Tunable System .**

(3) Lower Detection Limits, Improved Specificity by Time Gating
- **Characterize How Well a Gated-OMA Functions As Compared to an Emission Monochromator**

Laser Induced Fluorescence Sensors (cont.)

Tasks

(4) Downhole Frequency Doubling
- **Use Powdered Doubling Crystals**
- **Proof-of-Concept Performed**
- **Characterize and Optimize Doubling Process**

(5) Alternate Wavelength-Selectable Laser Sources
- **Raman Shifters**
- **Optical Parametric Oscillators (OPOs)**
- **Ti:Sapphire**

APPROACH

1. Laser Photofragmentation

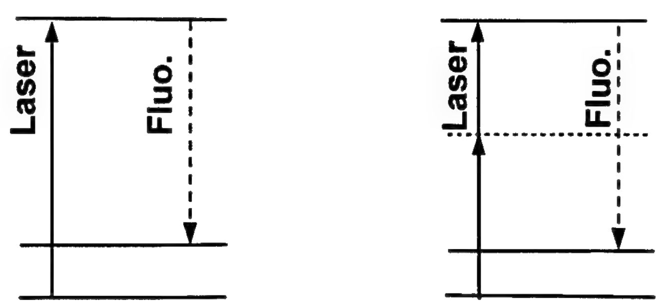
$$R\text{-}NO_2 \xrightarrow{h\nu_1} R + NO_2$$

2. Fragment Detection

$$NO_2 \xrightarrow{h\nu_2} NO^+ + O$$
$$NO_2 \xrightarrow{h\nu_2} NO^* + O$$

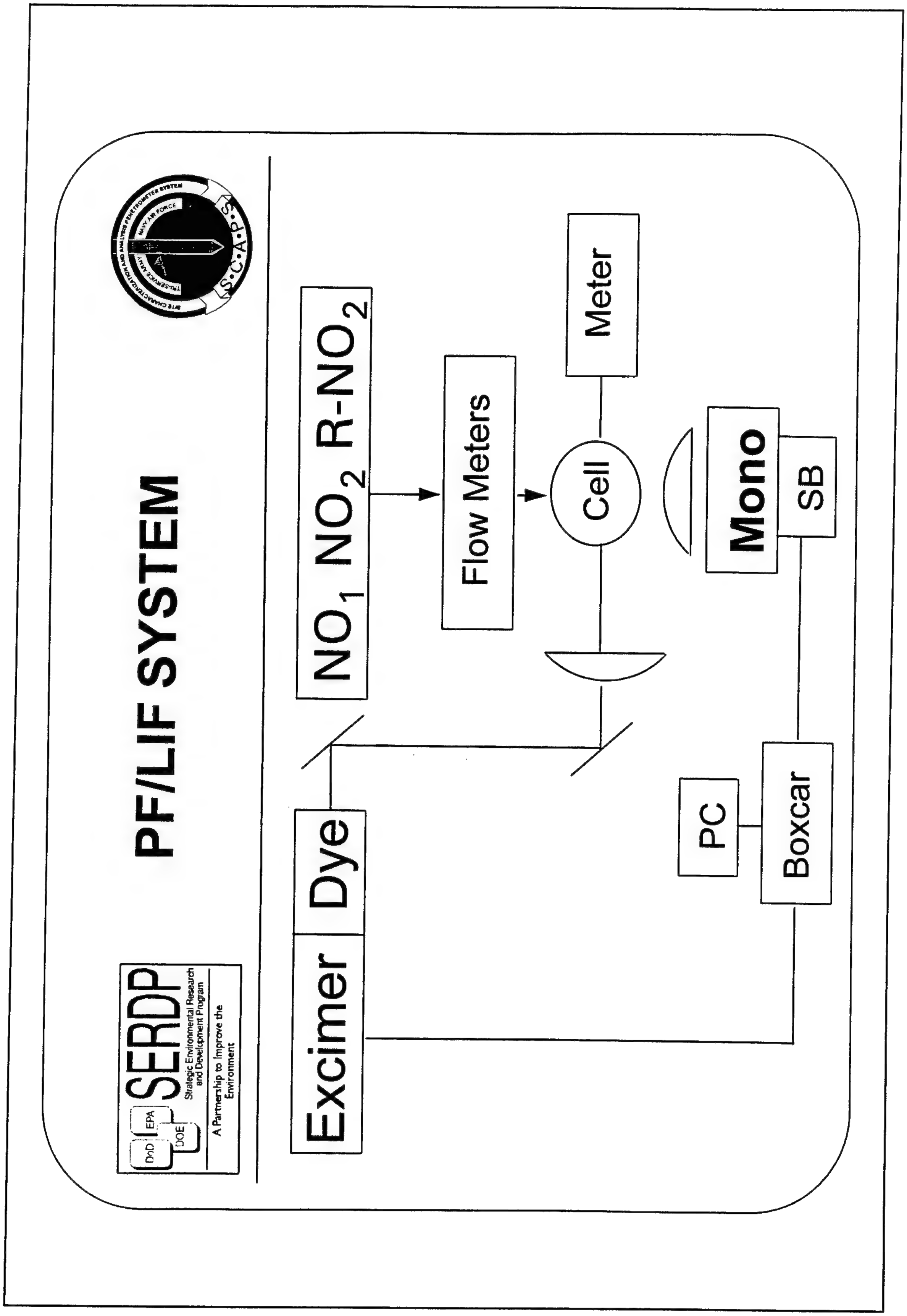
where $h\nu_1 = h\nu_2$

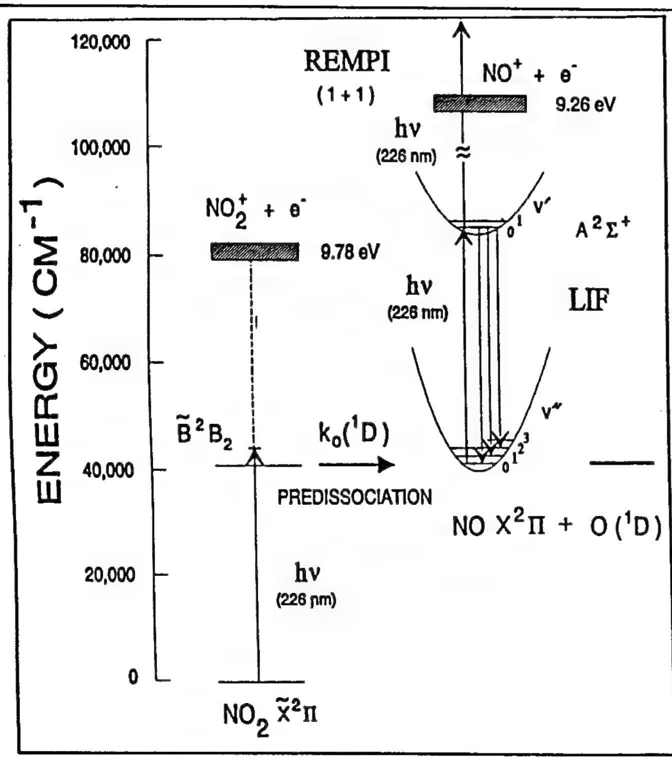
SINGLE AND MULTIPHOTON EXCITED FLUORESCENCE



High Background
High Scatter

Low Background
No Scatter


PF/LIF SYSTEM
SERDP
Strategic Environmental Research and Development Program
A Partnership to Improve the Environment
DoD
EPA
DOE
S•C•A•P•S
NO$_1$ NO$_2$ R-NO$_2$
Flow Meters
Cell
Meter
Mono
SB
Excimer
Dye
PC
Boxcar



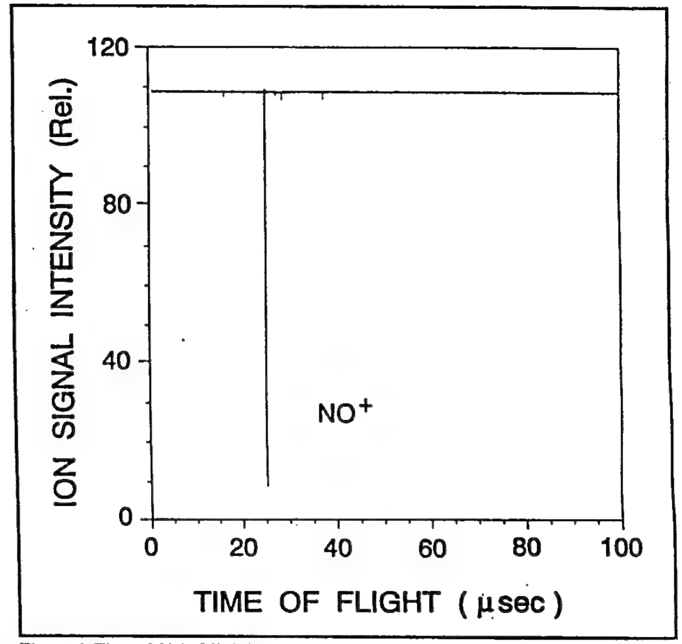
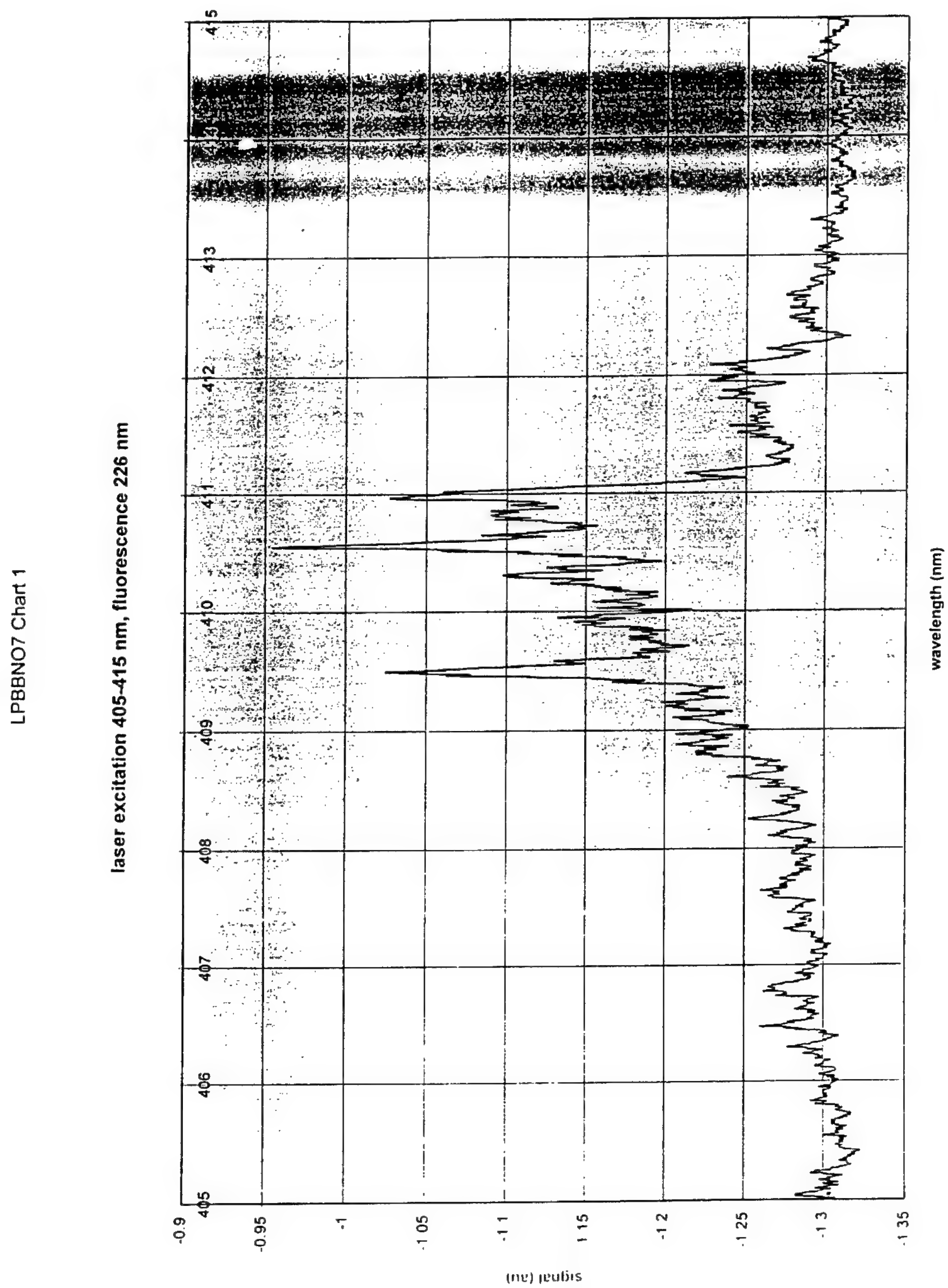


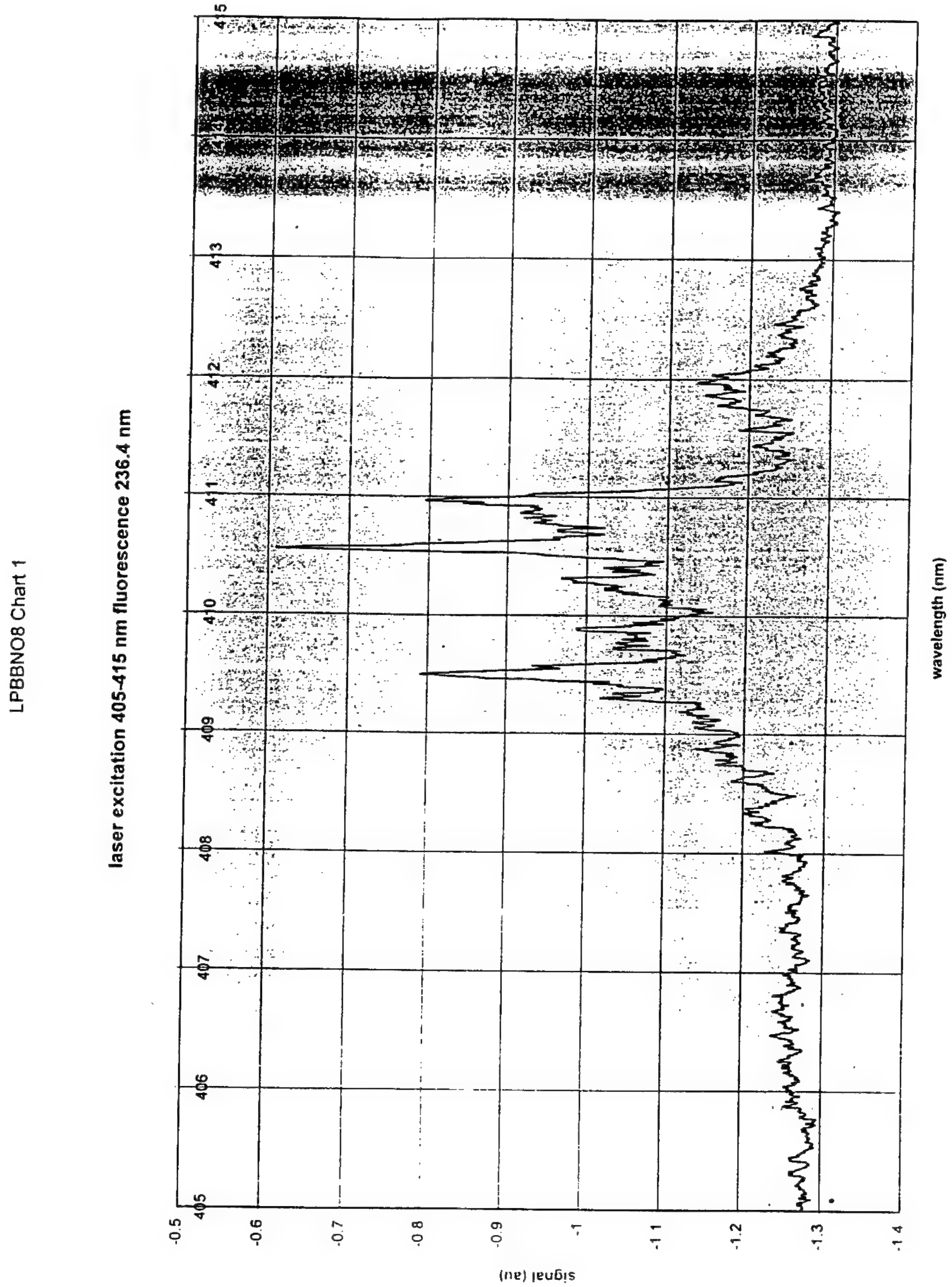
Figure 4. Time-of-flight REMPI spectrum of NO generated from DMNA. Signal generated from 226nm excitation of DMNA (~100µJ).

Table 1
Limits of Detection for Various Compounds Studied Using the 226nm Laser Photofragmentation/REMPI Technique with NO Detection

Compound	Limit of Detection (ppb)
NO	8
NO_2	240
CH_3NO_2	1000
DMNA	450
	(2000)*
RDX	8
TNT	24
Nitrobenzene	2400

*Limit of detection obtained by laser-induced fluorescence of NO via its $A^2\Sigma^+$ - $X^2\Pi$ transition


LPBBNO7 Chart 1
laser excitation 405-415 nm, fluorescence 226 nm
signal (au)
wavelength (nm)
-0.9
-0.95
-1
-1.05
-1.1
-1.15
-1.2
-1.25
-1.3
-1.35
405
406
407
408
409
410
411
412
413
415


LPBBNO8 Chart 1
laser excitation 405-415 nm fluorescence 236.4 nm
signal (au)
-0.5
-0.6
-0.7
-0.8
-0.9
-1
-1.1
-1.2
-1.3
-1.4
wavelength (nm)
405
406
407
408
409
410
411
412
413
415

Army Research Laboratory

SENSOR DEVELOPMENT WORKSHOP
29-30 August 1995
U.S. Army Corps of Engineers
Waterways Experiment Station

LASER-INDUCED FLUORESCENCE SENSORS

R.C Sausa
U.S. Army Research Laboratory
AMSRL-WT-PC
Aberdeen Proving Ground, MD 21005

Level of Support: FY94: 40K, FY95: 20K

OBJECTIVE

Develop and Deploy Advanced Optical Sensors Based on Laser Photofragmentation Laser-Induced Fluorescence for Rapid and Real-Time Site Characterization and Analysis

Army Research Laboratory

LASER PHOTOFRAGMENTATION/ LASER-INDUCED FLUORESCENCE

* Utilizes one laser to both fragment the target molecule and detect the characteristic fragments by laser-induced fluorescence.

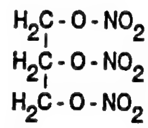
* System utilizes an optical fiber to transmit the laser radiation and an interference filter/PMT combination or optical multichannel analyzer for detection.

TECHNICAL PROGRESS

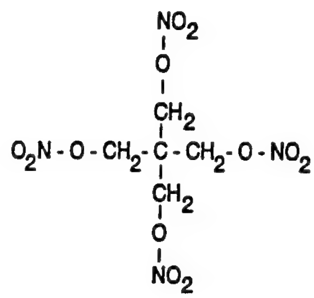
(Accomplishments)

- Designed & constructed LP/LIF cell
- Performed literature search. Reviewed pertinent papers & started writing review article on laser-based techniques for detection of nitrocompounds including energetic materials (analytical chemistry)
- Determined LODs of various nitrocompounds using LP/one-photon LIF of NO (a-x)(0,0) band near 26 nm
- Determined LODs of NO & NO_2 by two-photon LIF of NO (a-x) transitions using laser radiation near 452 nm
- Wrote & tested multi-parameter computer program for spectral simulation of NO (a-x) band
- Initiated system design of prototypical system established contact with WES for field testing/use
- Three open literature

Army Research Laboratory



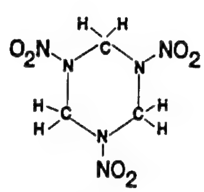
Nitroglycerine



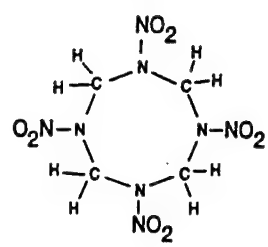
Pentaerytritol tetranitrate

$CH_3\text{-}NO_2$

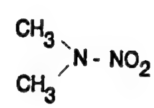
Nitromethane



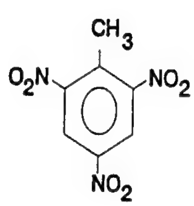
RDX



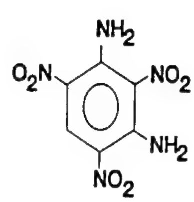
HMX



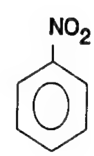
DMNA



TNT



DATB



Nitrobenzene

Army Research Laboratory

APPROACH

1. *Laser Photofragmentation*

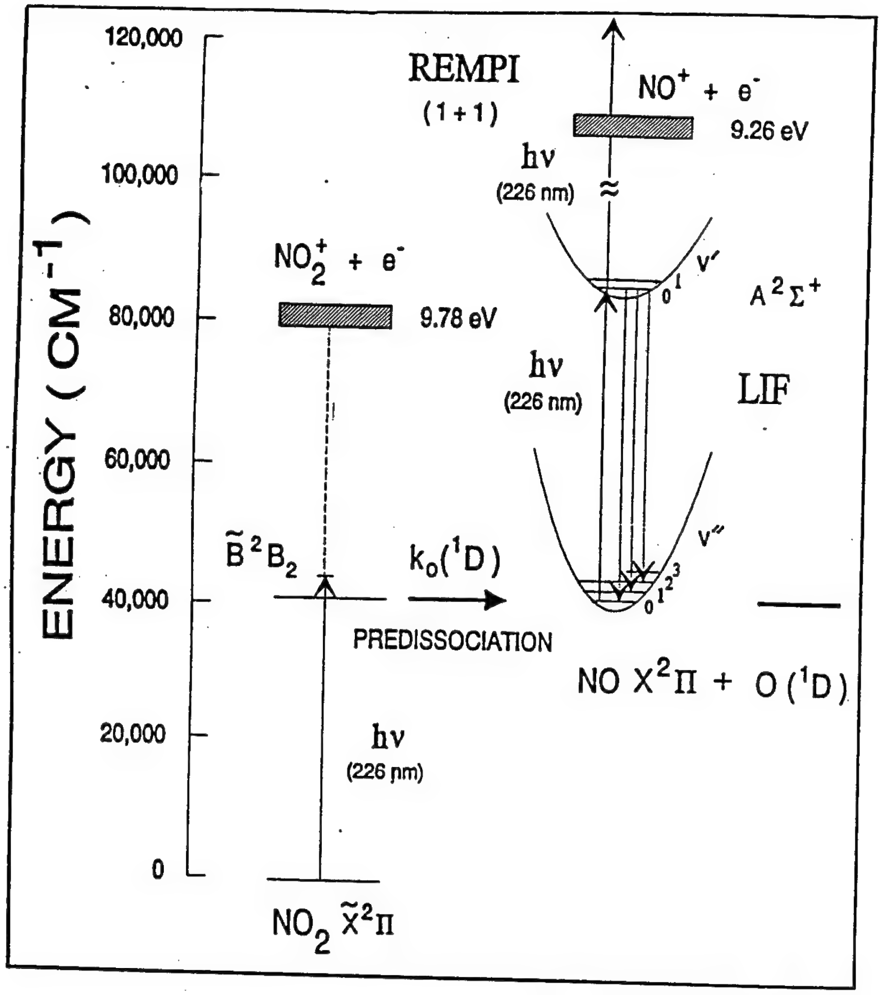
$$R\text{-}NO_2 \xrightarrow{h\upsilon_1} R + NO_2$$

$$NO_2 \xrightarrow{h\upsilon_2} NO + O$$

2. *Fragment LIF Detection*

$$NO \xrightarrow{h\upsilon_3} NO^*$$

where $h\upsilon_1 = h\upsilon_2 = h\upsilon_3$


120,000
100,000
80,000
60,000
40,000
20,000
0
ENERGY (CM^{-1})
REMPI
(1+1)
NO$^+$ + e$^-$
9.26 eV
hν
(226 nm)
NO_2^+ + e$^-$
9.78 eV
v'
$A^2\Sigma^+$
hν
(226 nm)
LIF
v"
$\tilde{B}^2B_2$
$k_o(^1D)$
PREDISSOCIATION
NO $X^2\Pi$ + O (^{1}D)
hν
(226 nm)
NO_2 $\tilde{X}^2\Pi$

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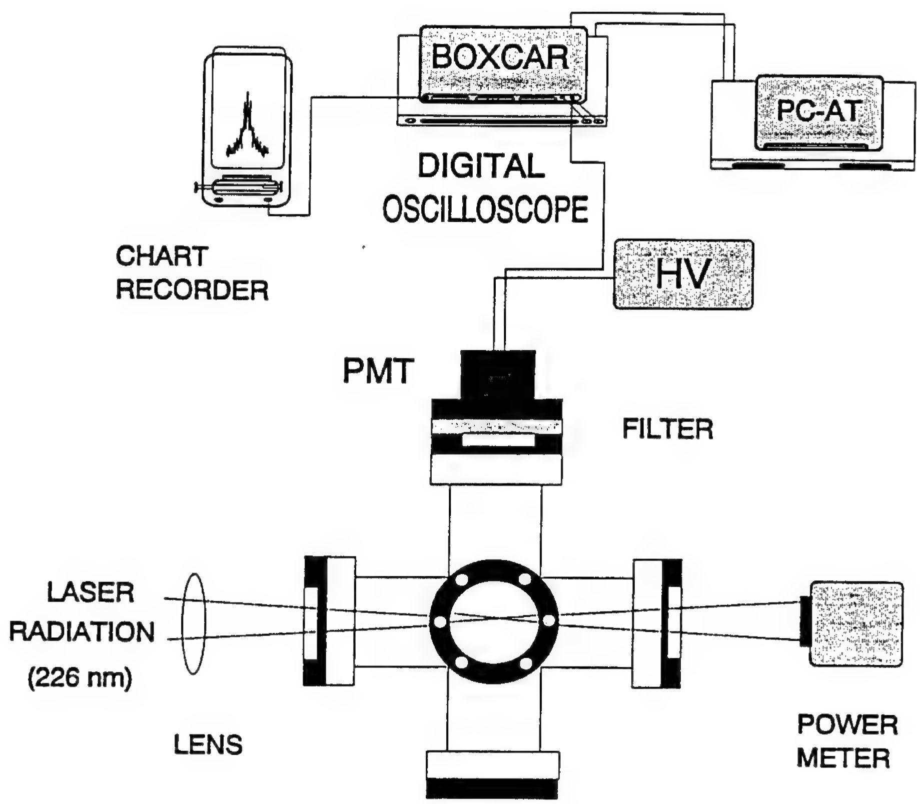
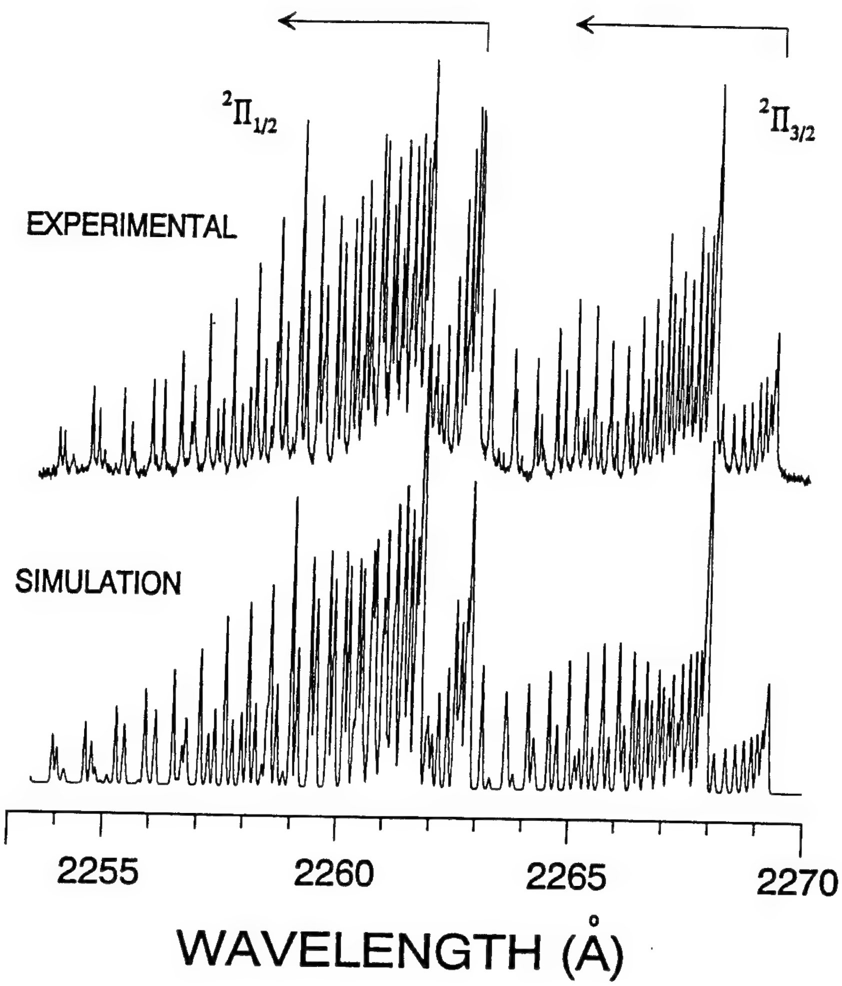
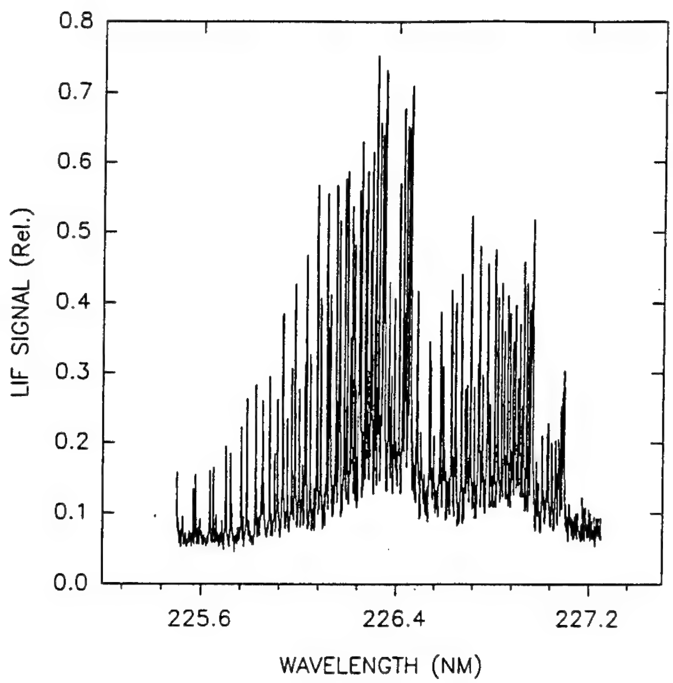


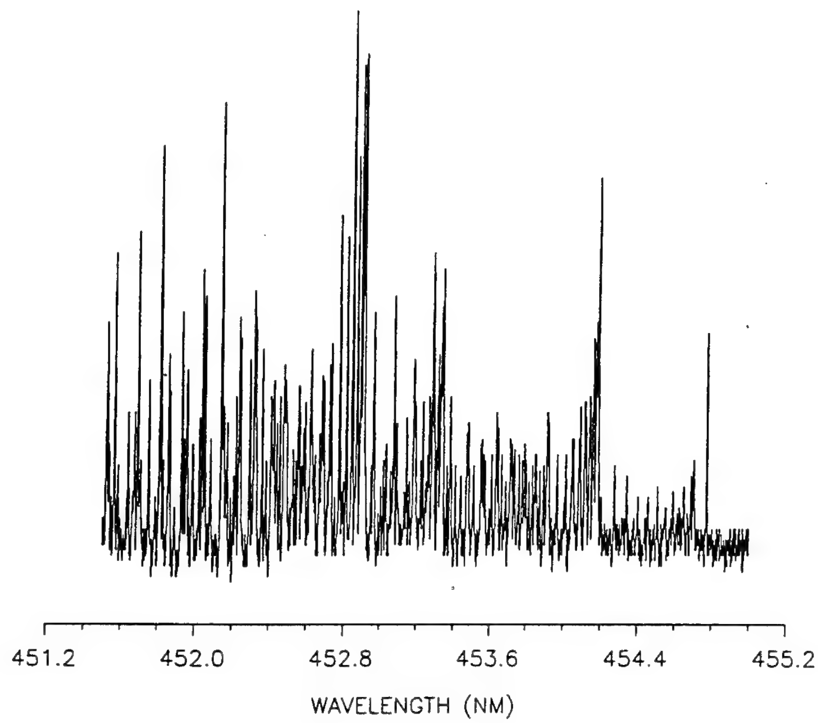
Army Research Laboratory



Army Research Laboratory



Army Research Laboratory



Limits of detection for various nitrocompounds studied using the technique of laser photofragmentation/ NO fragment detection by REMPI-TOF.

Compound	Limit of Detection (ppb)
NO	8, (1) [a]
NO_2	240, (22) [a]
CH_3NO_2	1000, (220) [a]
DMNA	450 (2000) [b]
RDX	8
TNT	24
Nitrobenzene	2400

[a] LODs obtained by NO REMPI using a pair of miniature electrodes.

[b] LOD obtained by LIF via the NO $A^2\Sigma^+ - X^2\Pi$ (0,0) transition.

PROPOSED RESEARCH

FY96 - 130K

(Labor, 110K, ½ manyr + postdoc, Equipment, 20K)

- Designed and construct prototypical system to couple with penetrometer probe
- Laboratory test, evaluate, and optimize system using site samples
- Field test sensor at sites designated by WES

ACKNOWLEDGEMENT

* Dr. Robert Pastel, U.S. Army Research Laboratory Postdoctoral Fellow.
* Professor Josef Simeonsson of the University of Iowa, Department of Chemistry.
* Dr. Ernesto Cespedes of the U.S. Army Engineer Waterways Experiment Station.
* Strategic Environmental Research Development Program on Site Characterization and Analysis Penetrometer System.

SERDP
Strategic Environmental Research and Development Program
A Partnership to Improve the Environment

RESEARCH AREA III FOR SENSOR

SCAPS

Milestones

	Schd	Reschd	Comp
• Complete development of laboratory FORS system	03/94	08/94	08/94
• Complete characterization of detection capabilities	09/94	12/94	12/94
• Complete fabrication of prototype FORS probe	03/95		03/95
• Complete design of resonance enhanced FORS probe	09/95		
• Complete fabrication of resonance enhanced FORS probe	12/95		
• Complete FORS software development	03/96		
• Complete field demonstration of resonance enhanced FORS probe	08/96	01/97	

SERDP

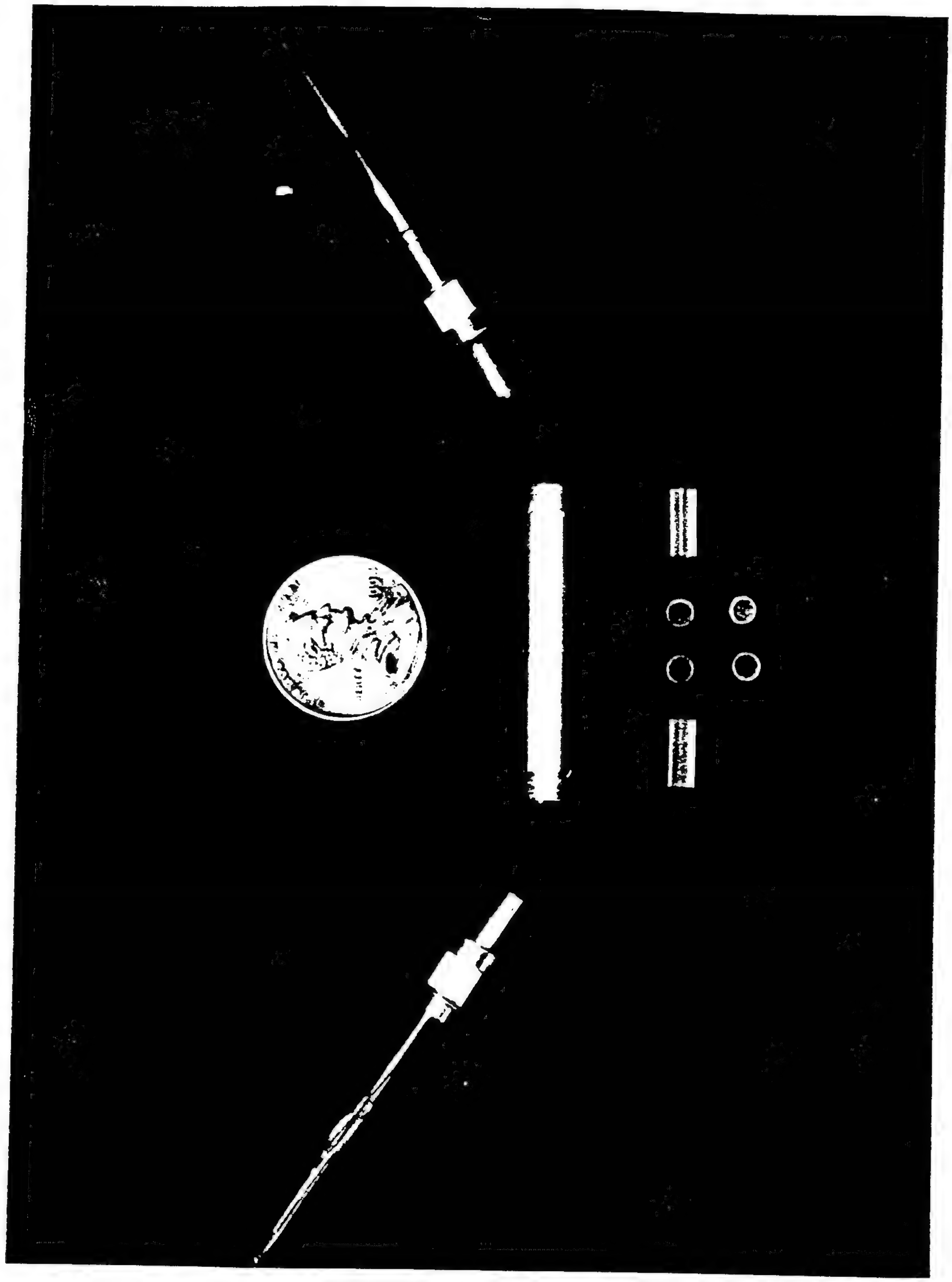
Advantages of Fiber Optic Raman Spectroscopy

1. Specificity
2. Simultaneous multicomponent analysis
3. Minimal Raman interferences from matrix
4. Remote
5. Real-Time
6. In-situ

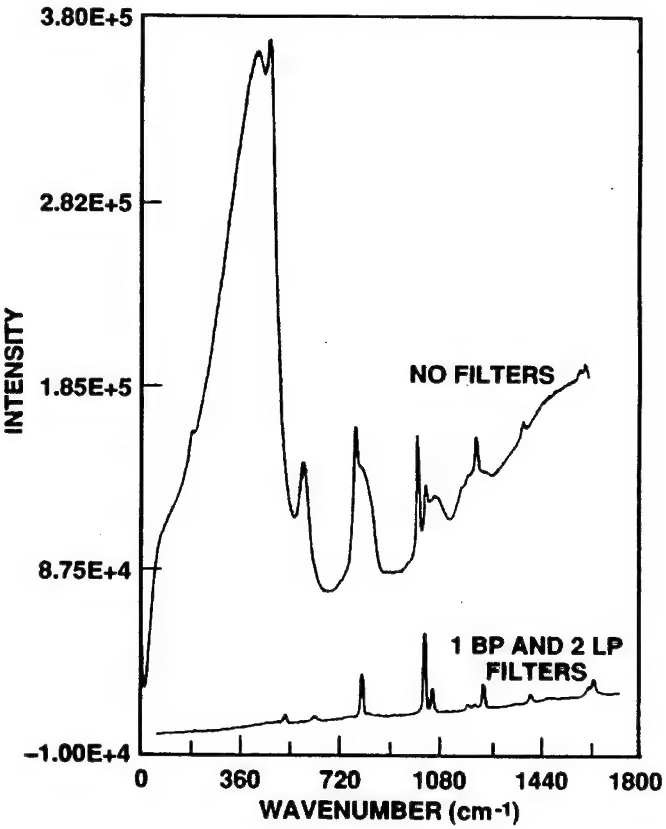
Technical Challenges

1. Interferences due to Raman emissions in optical fibers
2. Fluorescence interferences from matrix
3. Low sensitivity

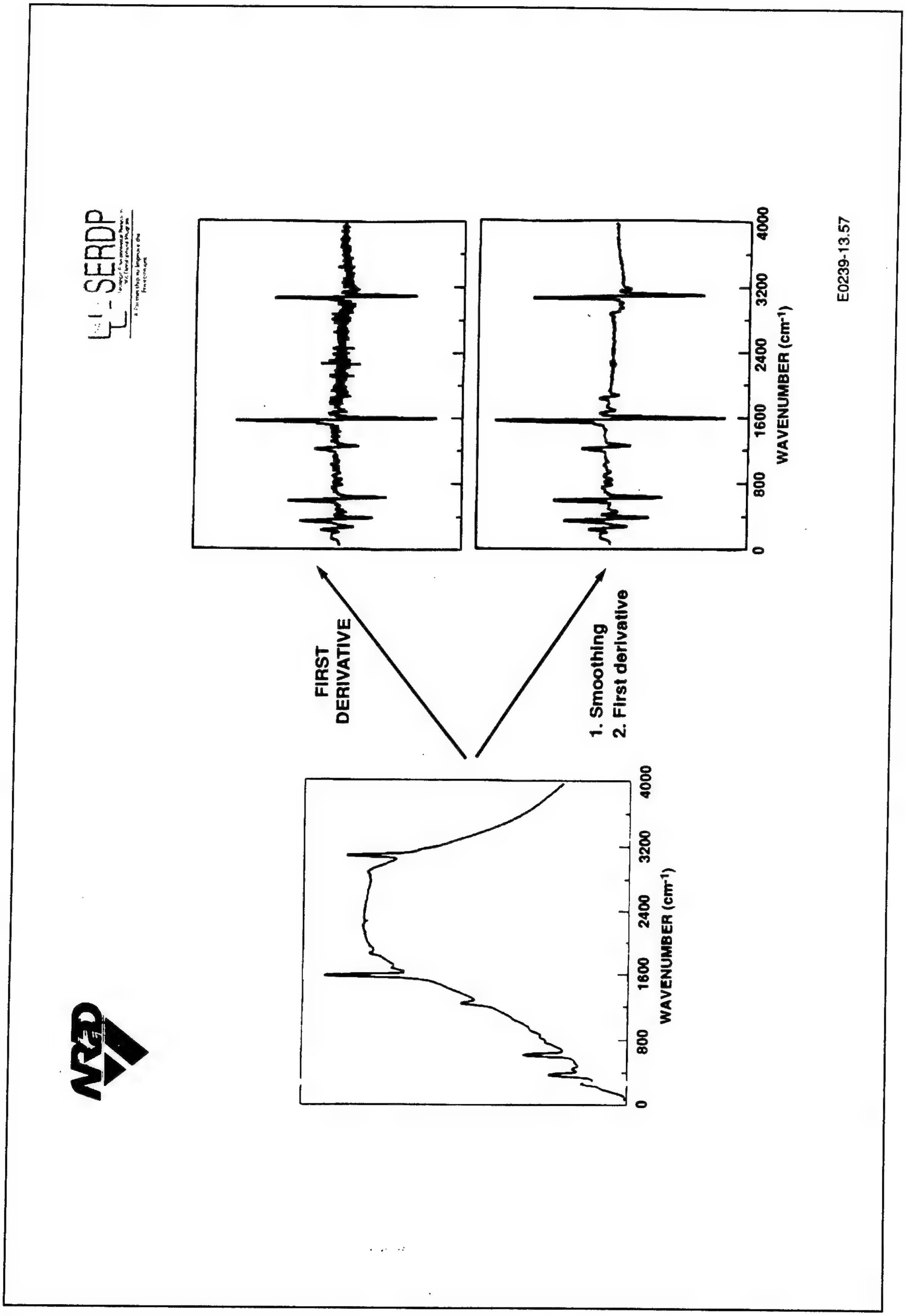
E0852-13.52



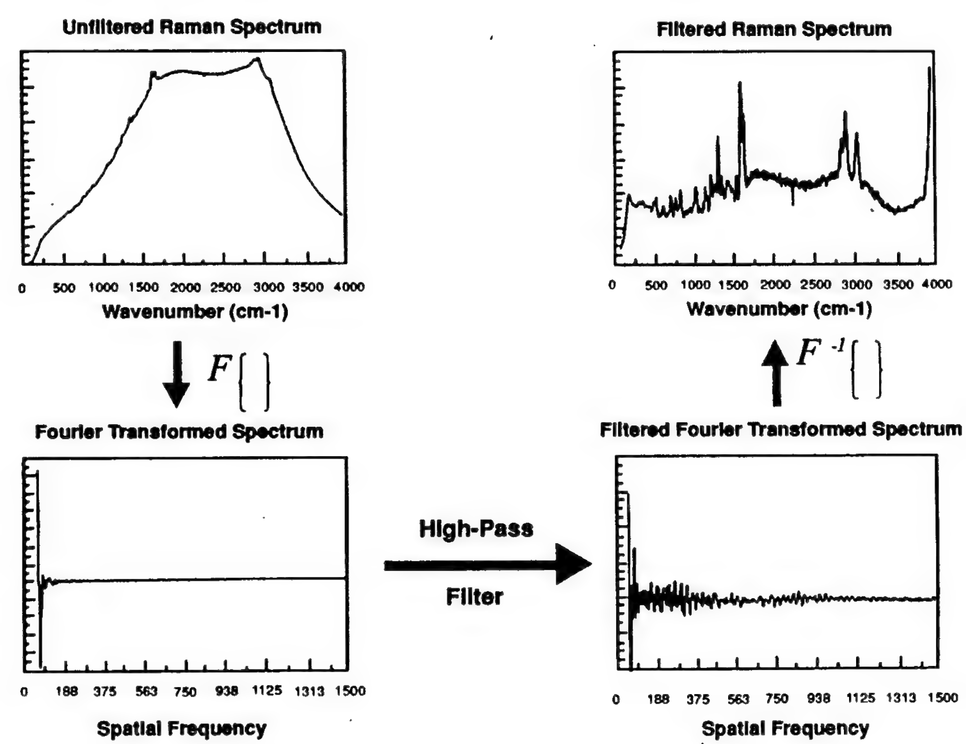
Reduction of Raman Emissions from the Optical Fibers



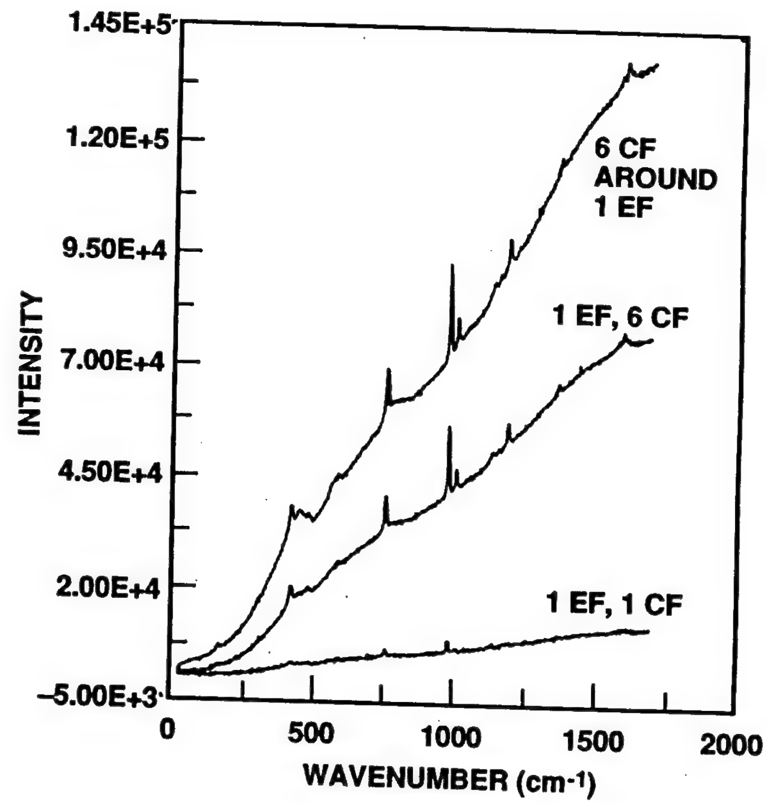
E0852-12.52


SERDP
0
800
1600
2400
3200
4000
WAVENUMBER (cm-1)
FIRST
DERIVATIVE
1. Smoothing
2. First derivative
0
800
1600
2400
3200
4000
WAVENUMBER (cm-1)
E0239-13.57

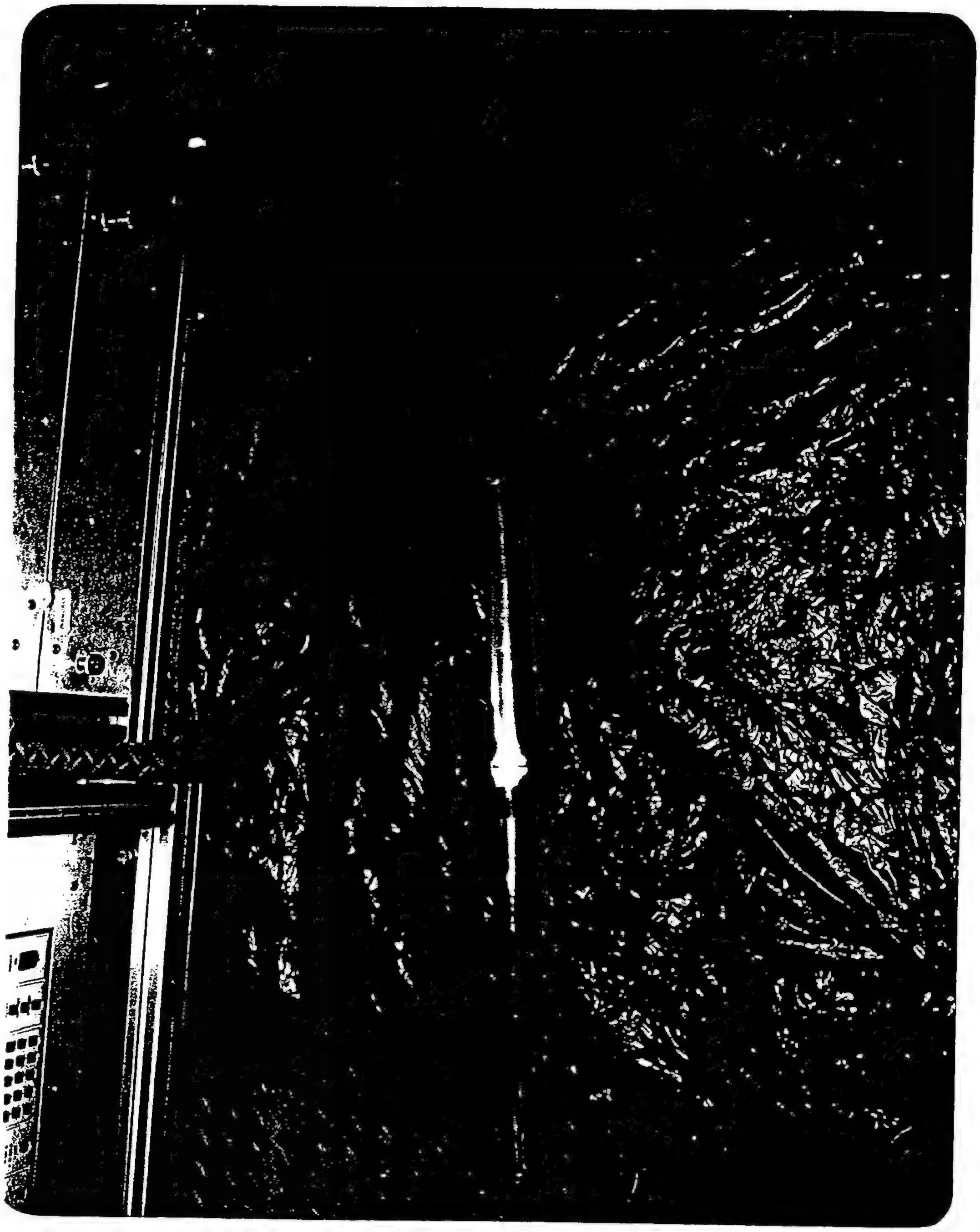
FFT Filtering

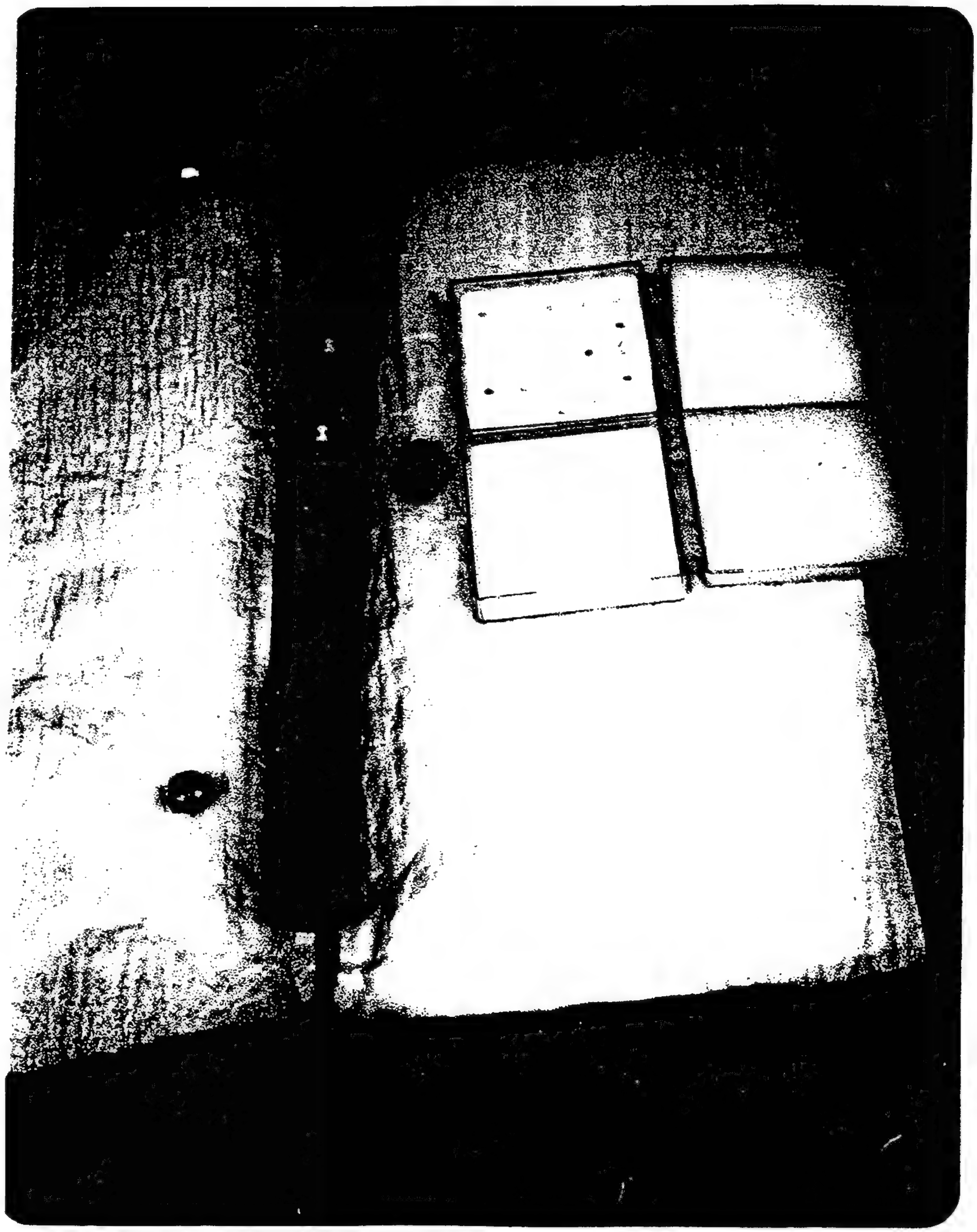


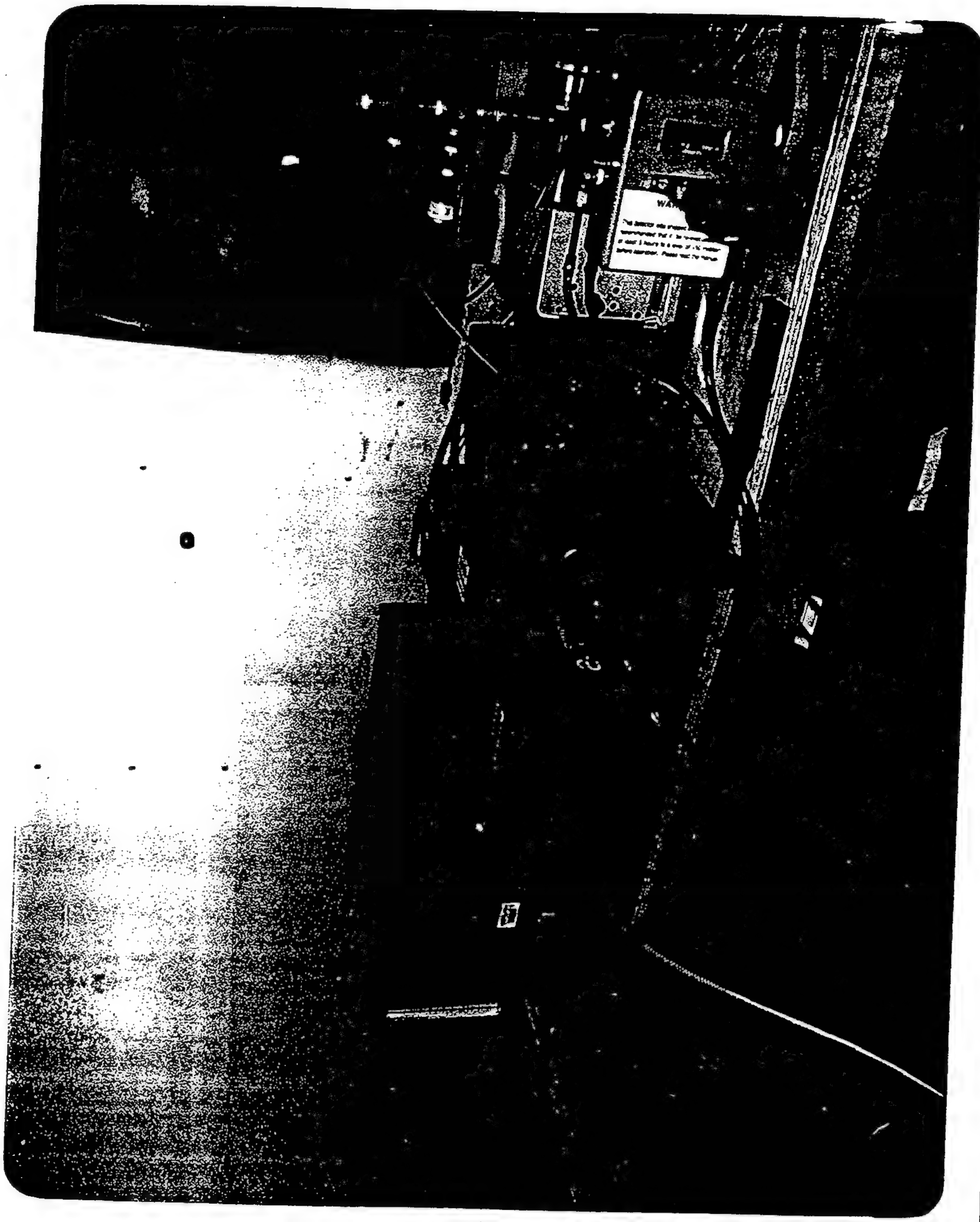
Multiple Collection Fibers to Improve Collection Efficiency

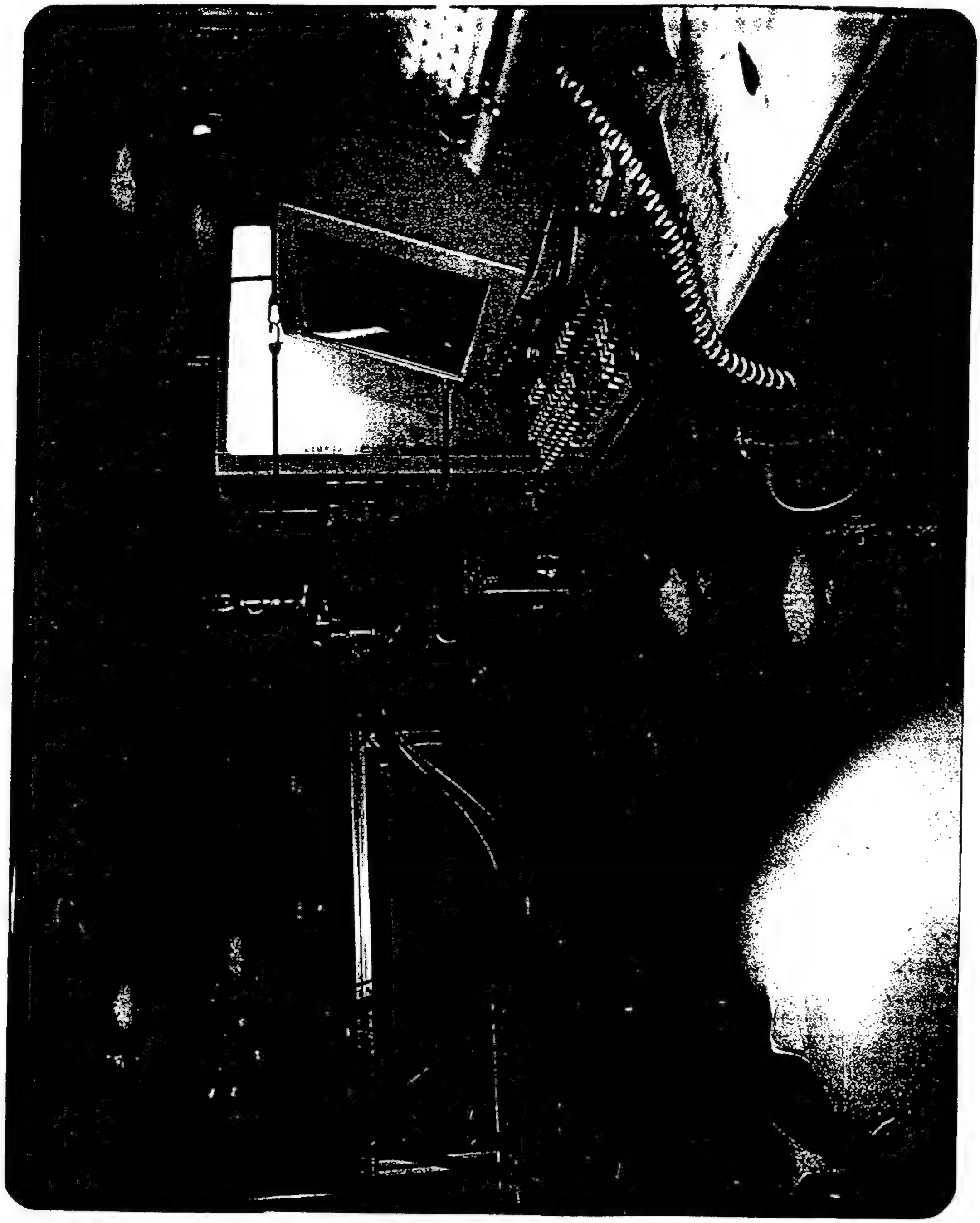


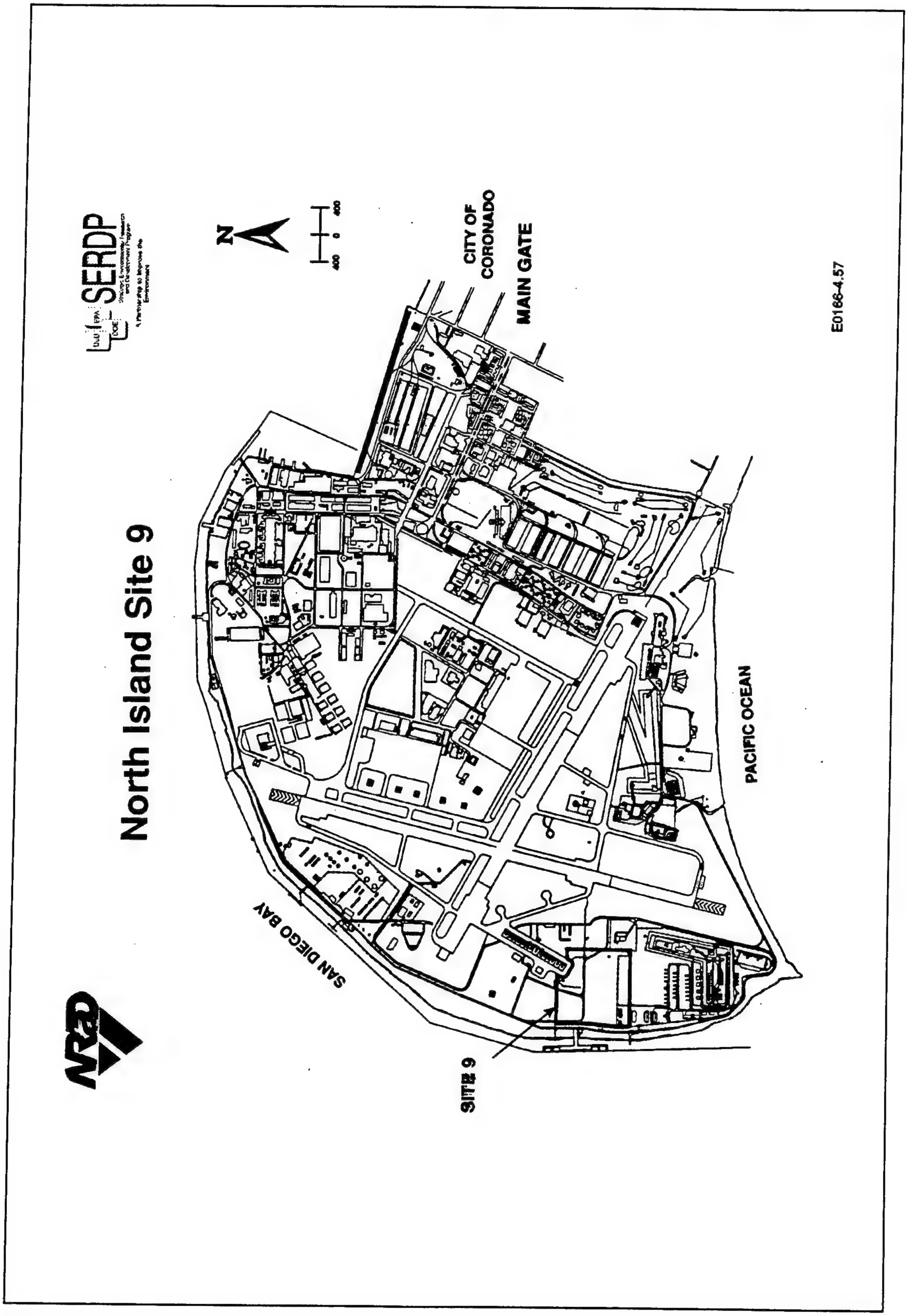
E0852-11.52



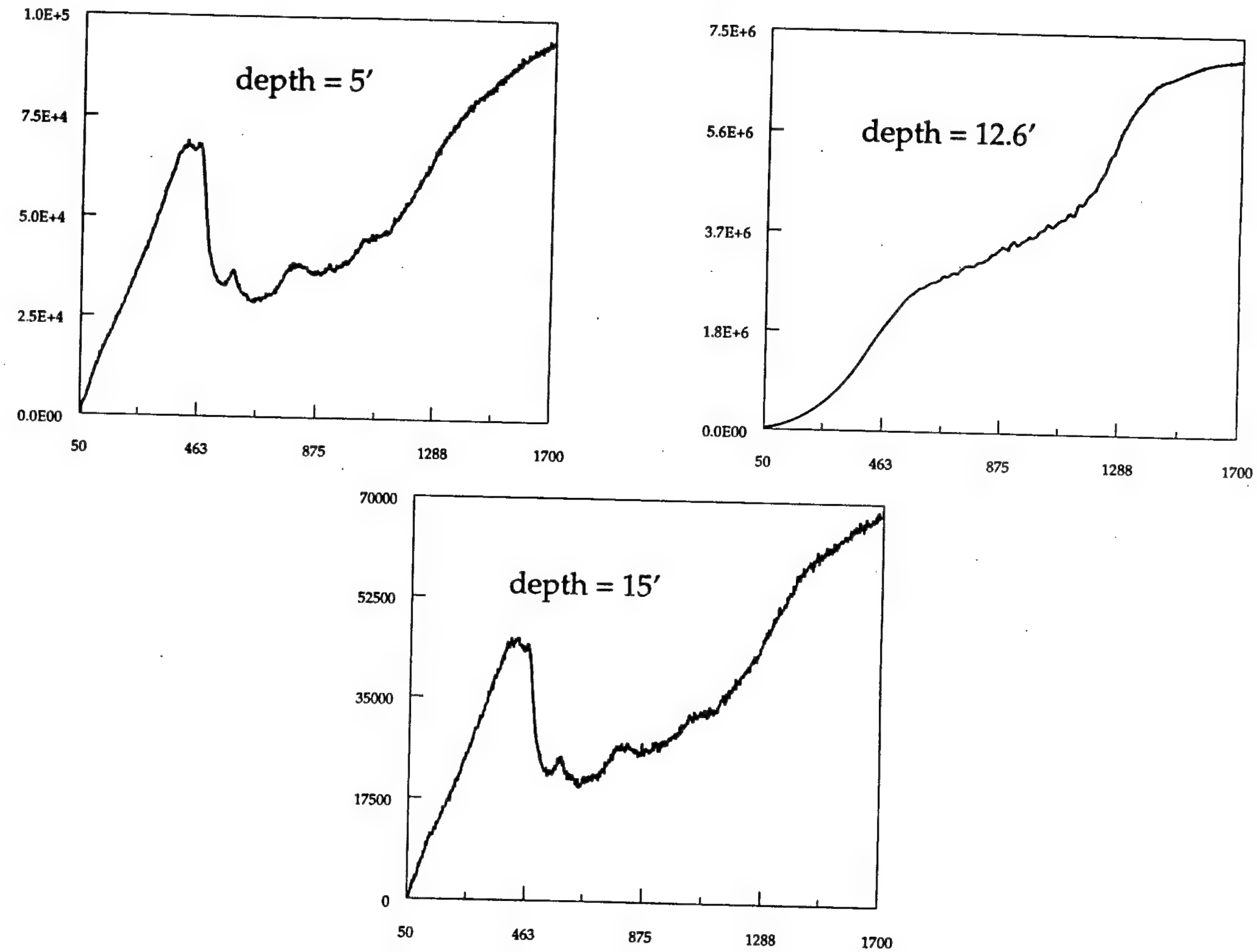


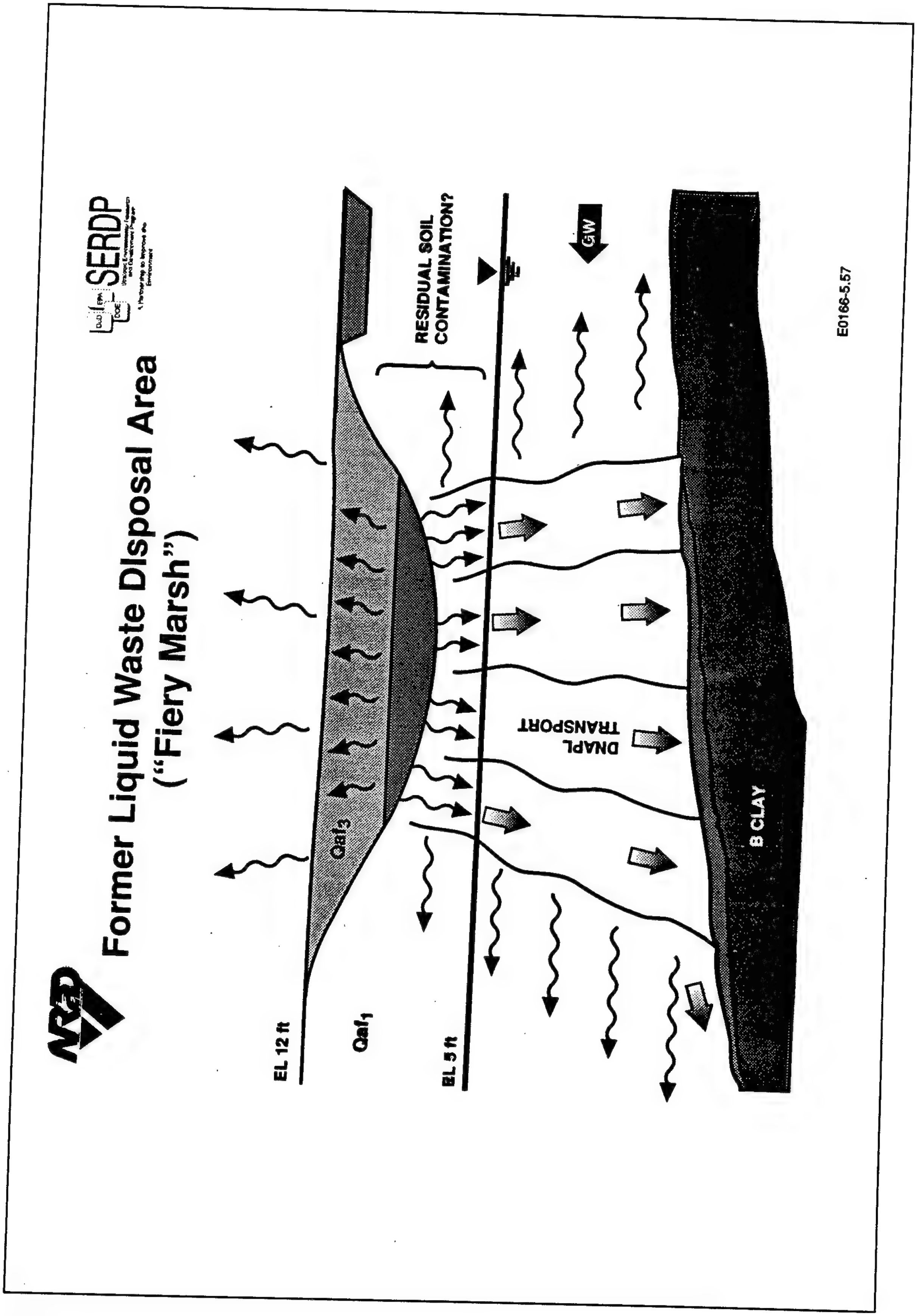


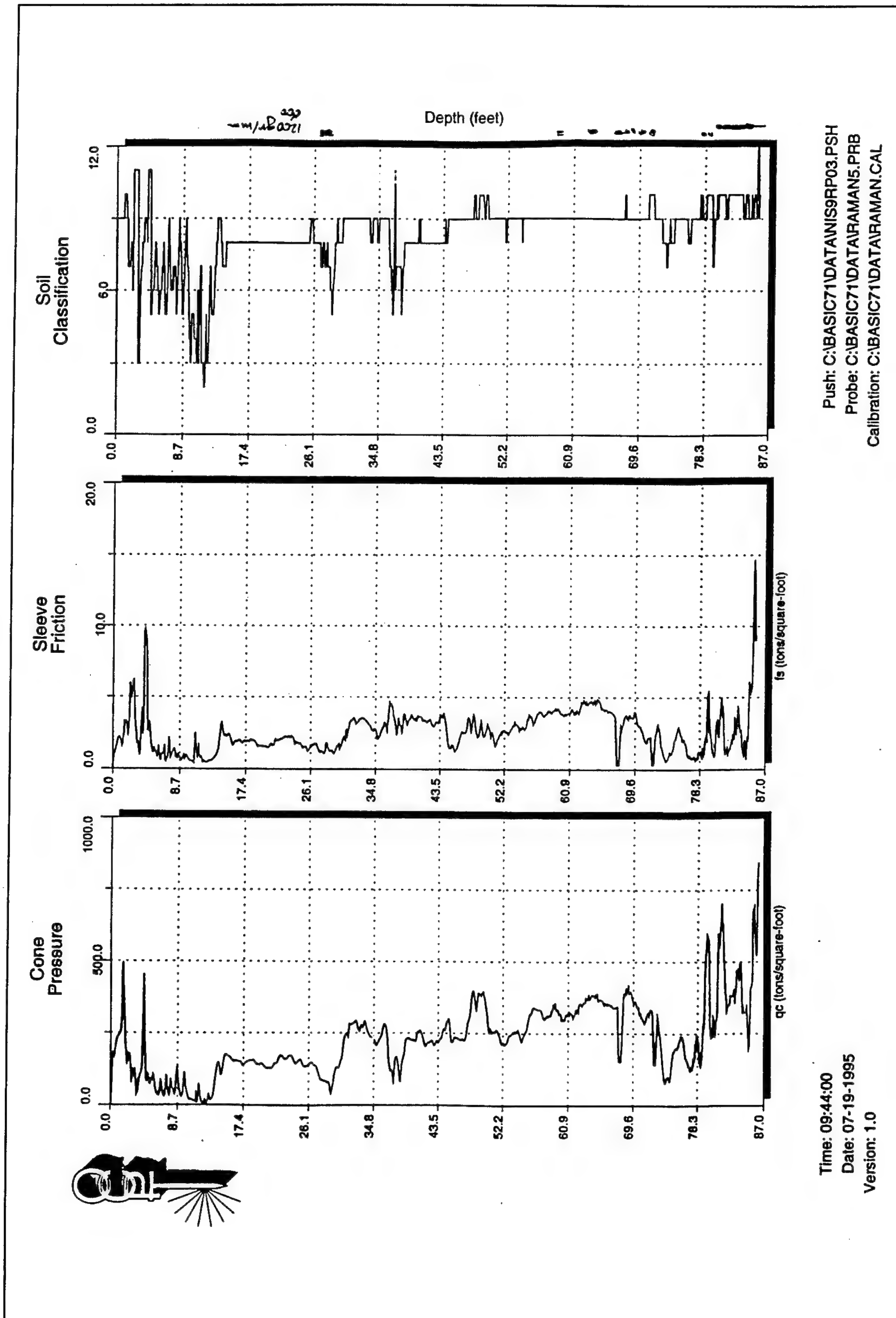


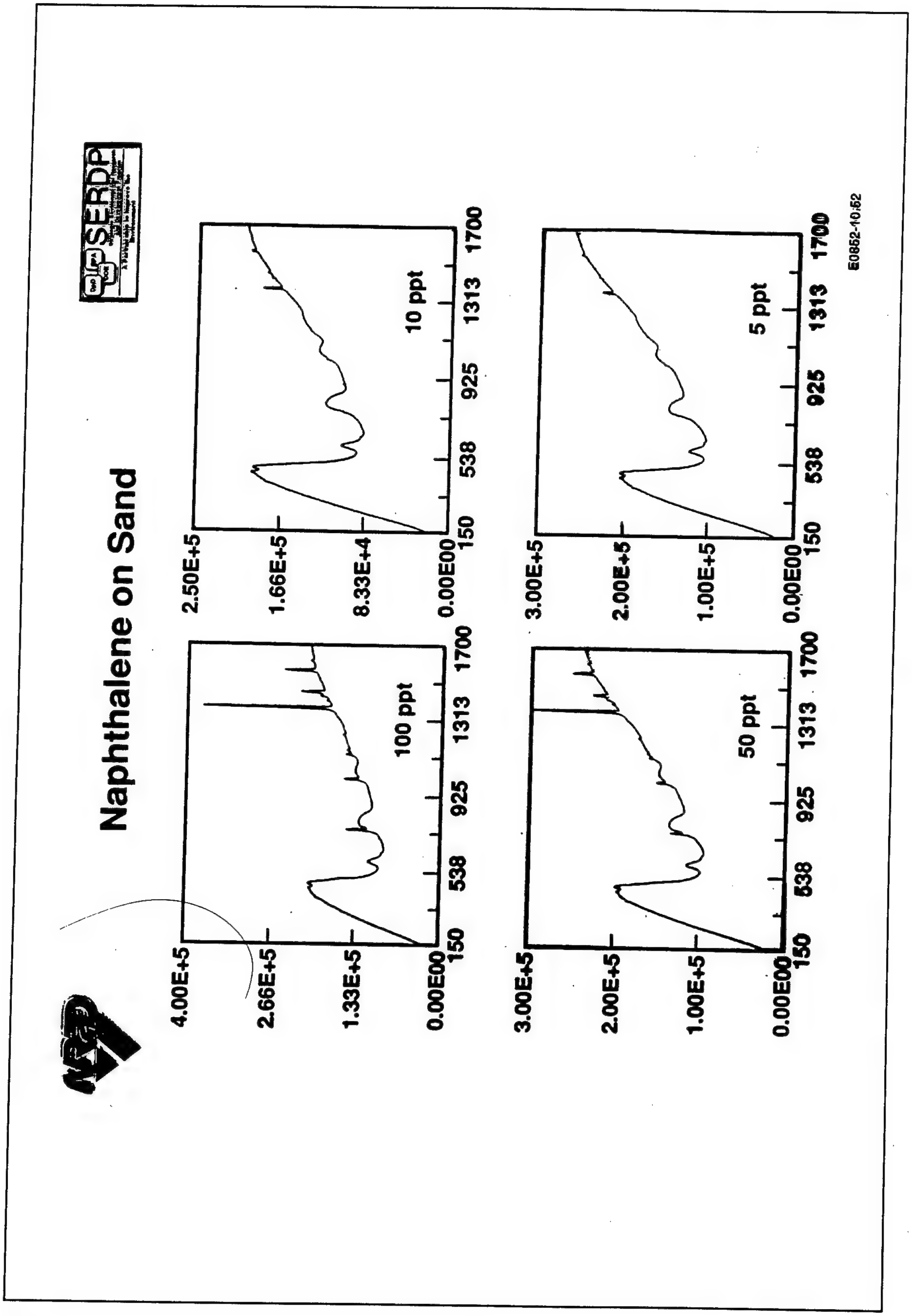

North Island Site 9
SERDP
N
400 0 400
CITY OF CORONADO
MAIN GATE
PACIFIC OCEAN
SAN DIEGO BAY
SITE 9
E0166-4.57

Spectra Obtained at the Fuel Farm

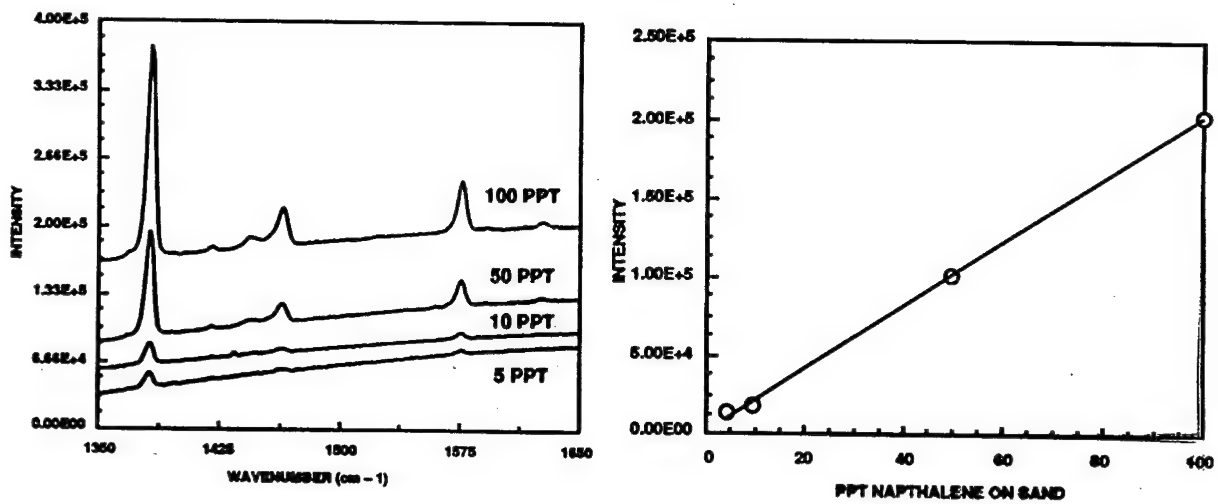



Former Liquid Waste Disposal Area
("Fiery Marsh")
SERDP
EL 12 ft
Qal1
Qal3
EL 5 ft
RESIDUAL SOIL
CONTAMINATION?
GW
DNAPL
TRANSPORT
B CLAY
E0166-5.57

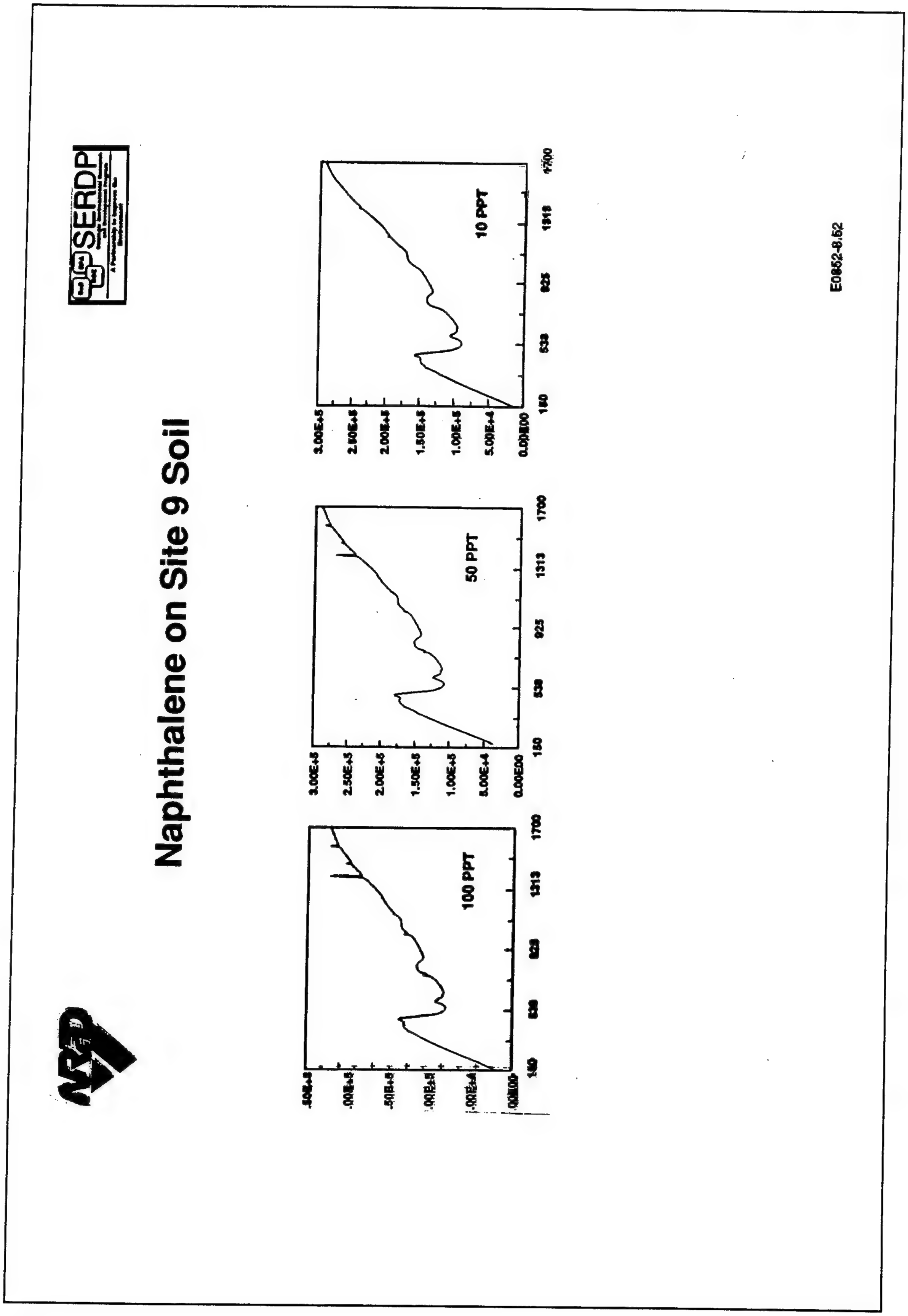

Depth (feet)
Soil Classification
Sleeve Friction
Cone Pressure
fs (tons/square-foot)
qc (tons/square-foot)
Push: C:\BASIC71\DATA\NIS9RP03.PSH
Probe: C:\BASIC71\DATA\RAMAN5.PRB
Calibration: C:\BASIC71\DATA\RAMAN.CAL
Time: 09:44:00
Date: 07-19-1995
Version: 1.0

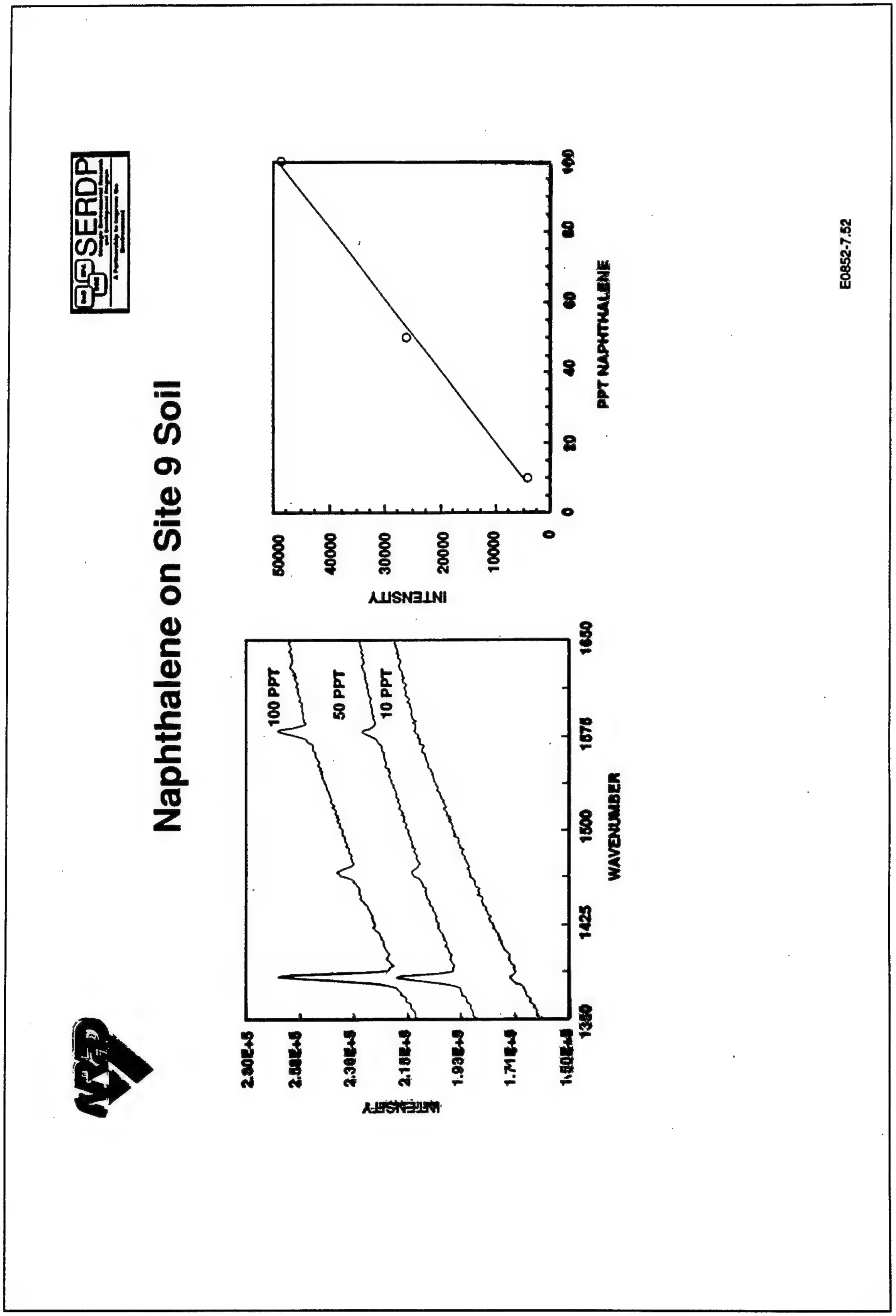

Naphthalene on Sand
SERDP
100 ppt
4.00E+5
2.66E+5
1.33E+5
0.00E00
150
538
925
1313
1700
10 ppt
2.50E+5
1.66E+5
8.33E+4
0.00E00
50 ppt
3.00E+5
2.00E+5
1.00E+5
0.00E00
5 ppt
E0852-10:52

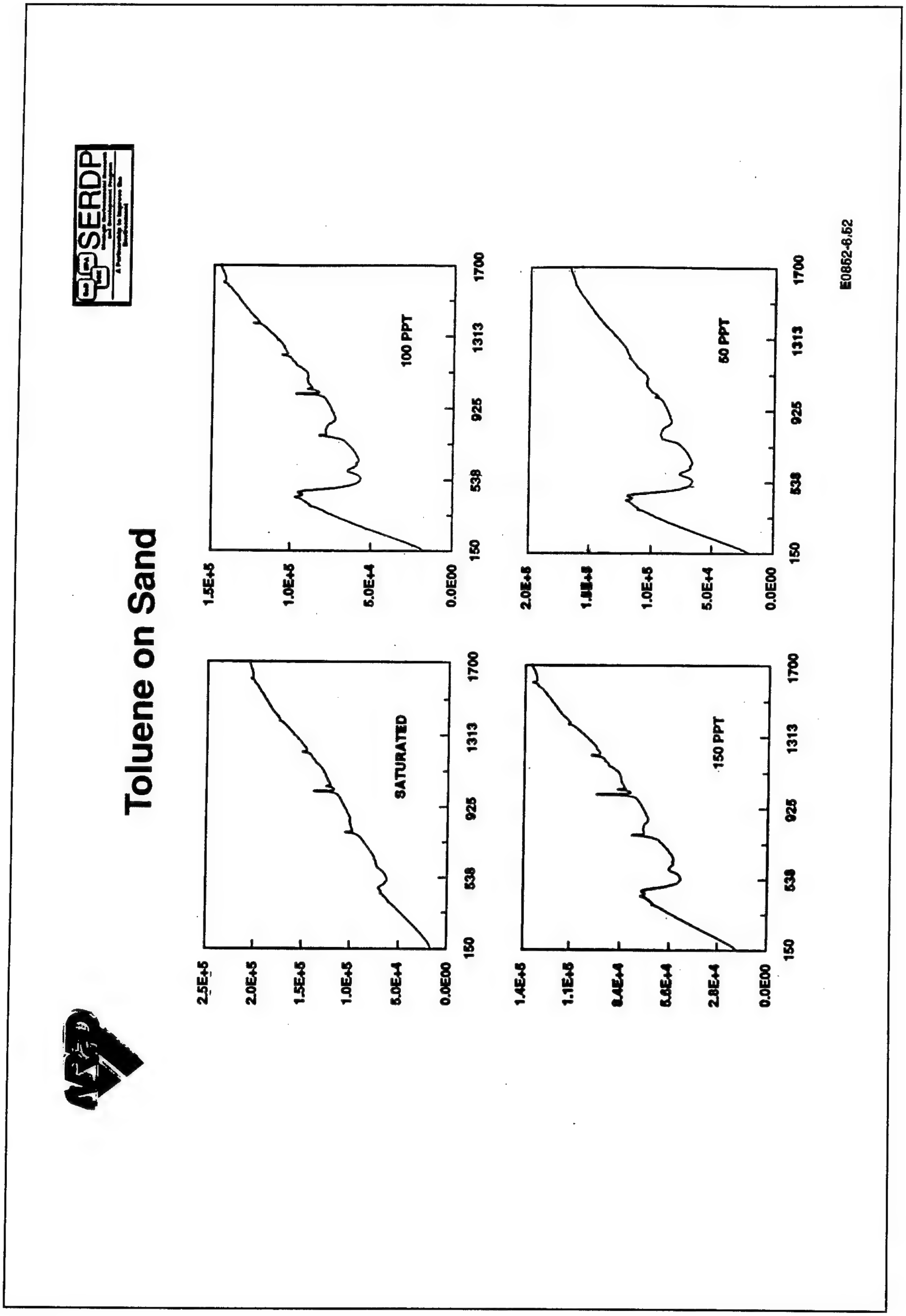
Napthalene on Sand



E0852-9.52

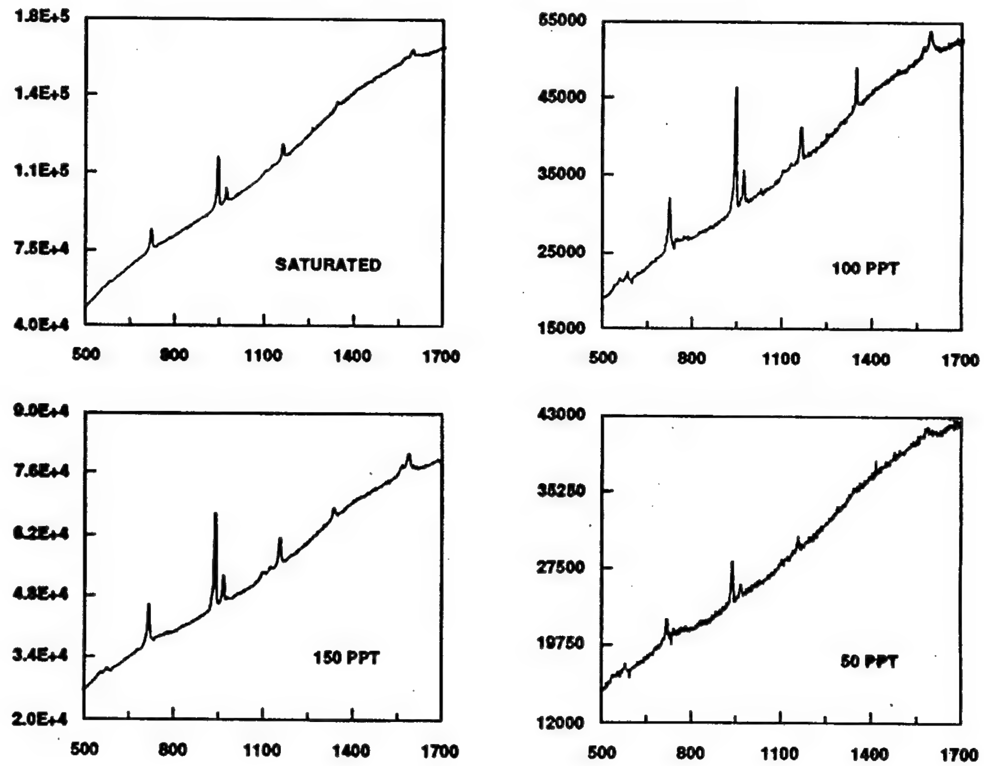

Naphthalene on Site 9 Soil
SERDP
100 PPT
50 PPT
10 PPT
3.00E+5
2.50E+5
2.00E+5
1.50E+5
1.00E+5
5.00E+4
0.00E00
150
538
925
1313
1700
E0852-8.52


Naphthalene on Site 9 Soil
SERDP
INTENSITY
WAVENUMBER
100 PPT
50 PPT
10 PPT
1350
1425
1500
1575
1650
INTENSITY
PPT NAPHTHALENE
0
20
40
60
80
100
10000
20000
30000
40000
50000
E0852-7.52

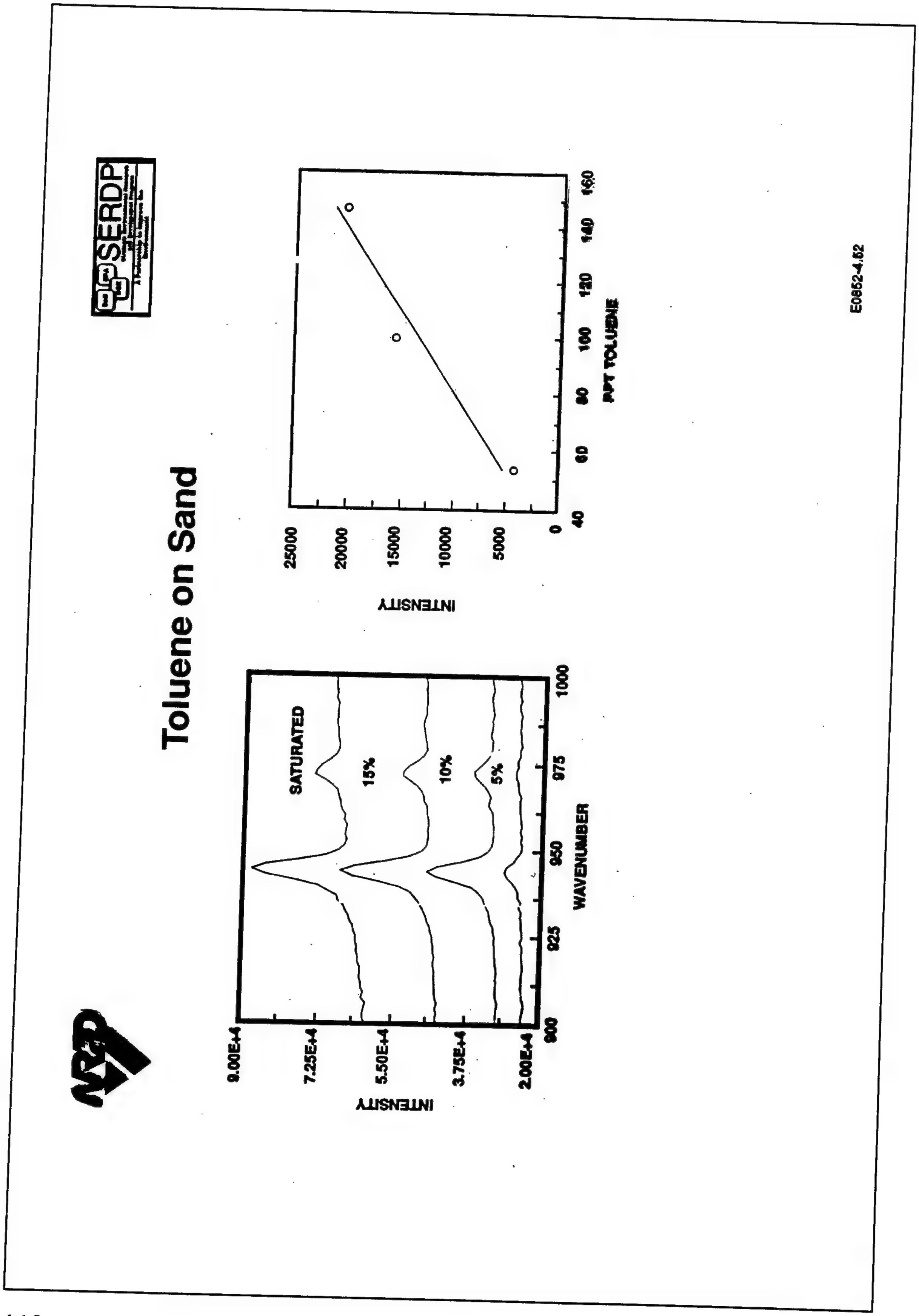


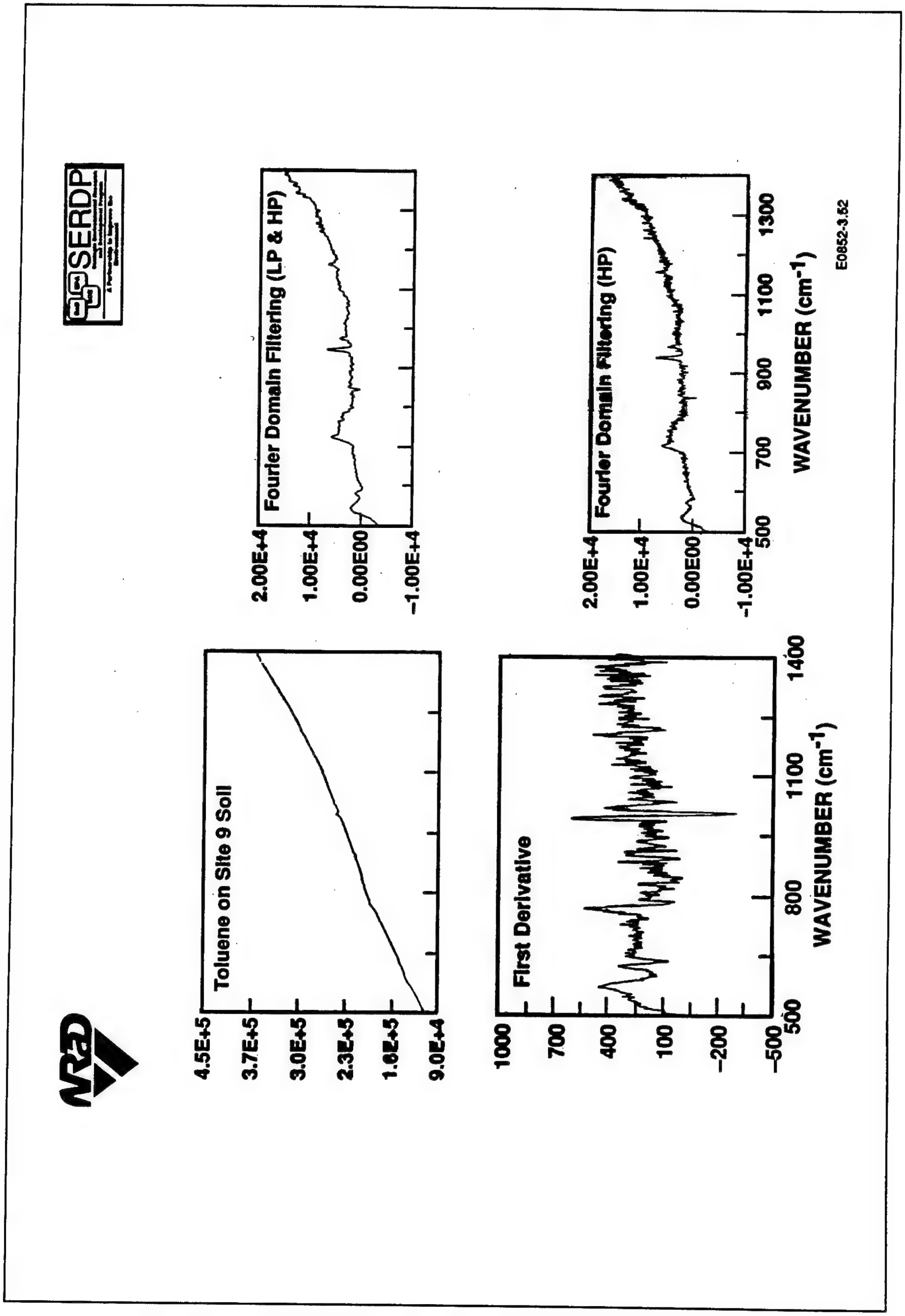
Toluene on Sand
SERDP
SATURATED
100 PPT
150 PPT
50 PPT
2.5E+5
2.0E+5
1.5E+5
1.0E+5
5.0E+4
0.0E00
1.4E+5
1.1E+5
5.6E+4
2.8E+4
150
538
925
1313
1700
E0862-6.52

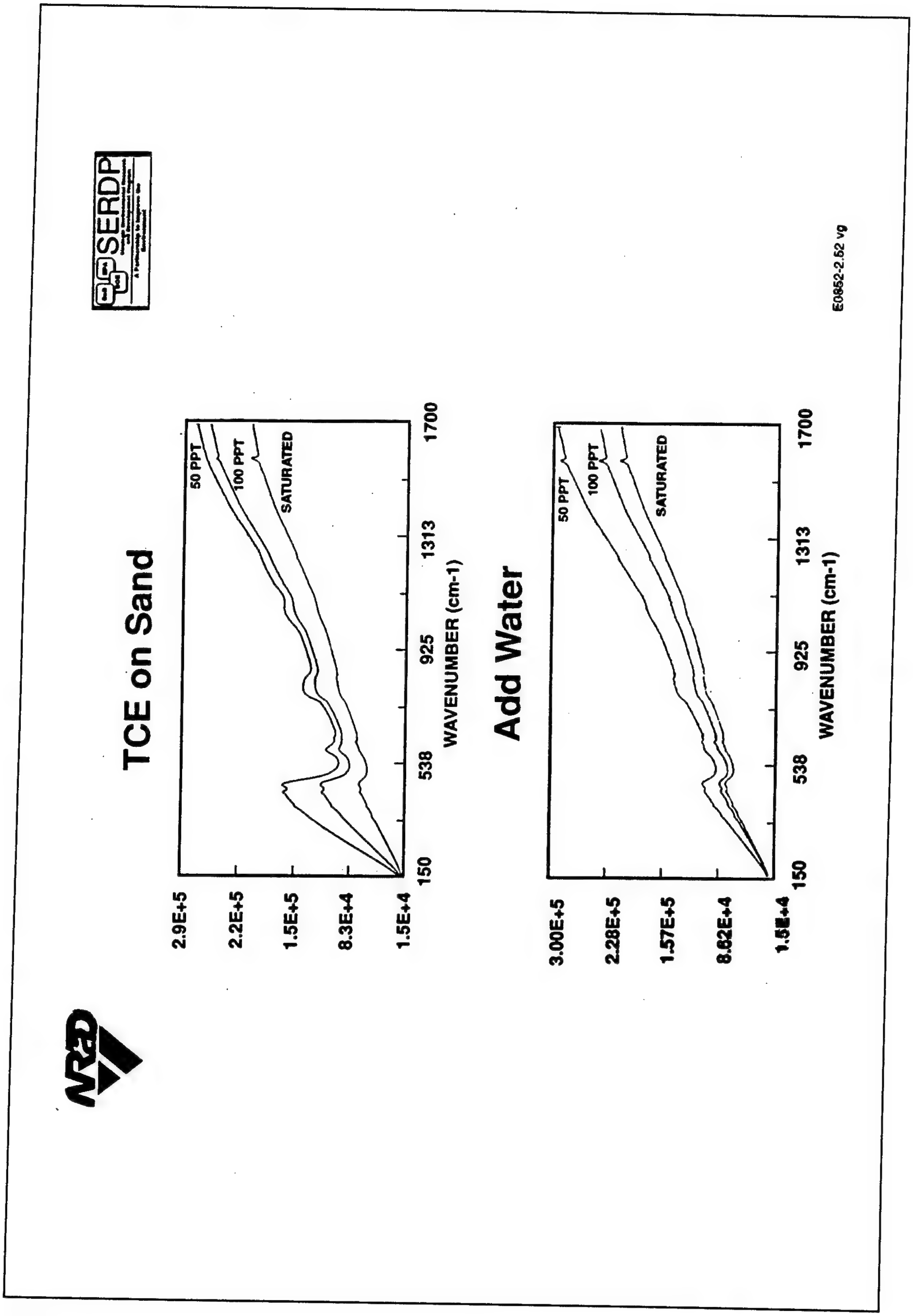
Toluene on Sand (Subtract Fiber Background)

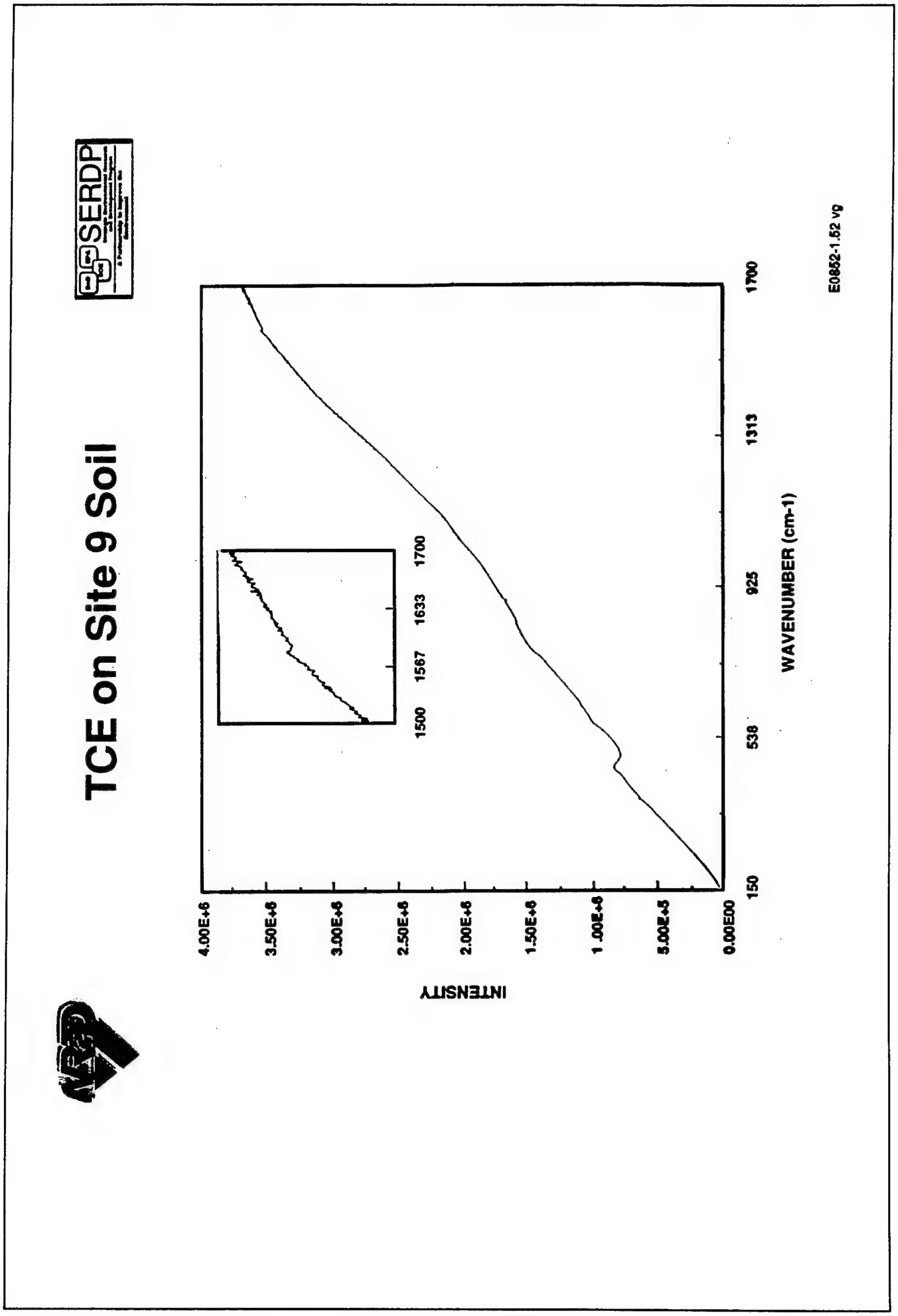


E0852-5.52


Toluene on Sand
SERDP
SATURATED
15%
10%
5%
9.00E+4
7.25E+4
5.50E+4
3.75E+4
2.00E+4
INTENSITY
900
925
950
975
1000
WAVENUMBER
25000
20000
15000
10000
5000
0
INTENSITY
40
60
80
100
120
140
160
PPT TOLUENE
E0852-4.82


SERDP
Toluene on Site 9 Soil
4.5E+5
3.7E+5
3.0E+5
2.3E+5
1.6E+5
9.0E+4
First Derivative
1000
700
400
100
-200
-500
500
800
1100
1400
WAVENUMBER (cm-1)
Fourier Domain Filtering (LP & HP)
2.00E+4
1.00E+4
0.00E00
-1.00E+4
Fourier Domain Filtering (HP)
2.00E+4
1.00E+4
0.00E00
-1.00E+4
500
700
900
1100
1300
WAVENUMBER (cm-1)
E0852-3.52


SERDP
TCE on Sand
50 PPT
100 PPT
SATURATED
2.9E+5
2.2E+5
1.5E+5
8.3E+4
1.5E+4
150
538
925
1313
1700
WAVENUMBER (cm-1)
Add Water
50 PPT
100 PPT
SATURATED
3.00E+5
2.28E+5
1.57E+5
8.62E+4
1.5E+4
150
538
925
1313
1700
WAVENUMBER (cm-1)
E0852-2.52 vg


TCE on Site 9 Soil
SERDP
INTENSITY
4.00E+6
3.50E+6
3.00E+6
2.50E+6
2.00E+6
1.50E+6
1.00E+6
5.00E+5
0.00E00
150
538
925
1313
1700
WAVENUMBER (cm-1)
1500
1567
1633
1700
E0852-1.52 vg

FLUORESCENCE

1. Near IR Excitation
2. Pico-second Raman Spectroscopy

1

LOW SENSITIVITY

1. Resonance Raman Spectroscopy
2. Surface Enhanced Raman Spectroscopy (SERS)

2

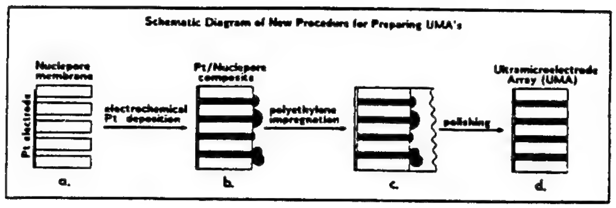
SURFACE ENHANCED RAMAN SPECTROSCOPY

Compound	Method of Adsorption	Substrate	Excitation (nm)
benzene	electrochemical	Ag	488, 514.5, 670
toluene	electrochemical	Ag	514.5
nitrate	electrochemical	Ag	670
TCE	electrochemical	biphase Cu	647, 676
TCE	1-octadecanethiol	Ag	647
benzene	1-octadecanethiol	Ag	647
xylenes	1-octadecanethiol	Ag	647
benzene	low temperature, 150K	Ag	488

3

Ultramicroelectrodes (UME):

1. Diameters less than 20 microns
2. Fast response time
3. Diminished Ohmic losses



4

Fiber Optic Raman Sensors

FOR Solvent Sensor

Principal Investigator: Dr Greg Gillispie,
Dakota Technologies, Inc./NDSU

Resonance Raman Approach

- Requires Tunable Laser or Multiple Wavelengths
- Proof-of-Concept Provided for TCE Detection

Raman Studies

- Use Nitrogen Laser With Subnanosecond Pulse
- Study Water Raman/Fluorescence Ratio

Raman Shifter Studies

- Vibrational and Rotational
  - Function of Gas, Pressure, and Pump Energy
  - Closely Spaced Output Lines in Ultraviolet
- Use of Solid State (Salt Crystal) Raman Shifter
- Using System With HPLC for Chemometric Studies

Fiber Optic Raman Sensors (cont.)

Research Questions:

- Amount of Resonance Enhancement As Function of Excitation Wavelength?
-- Use Raman Shifter

- Ability to Seperate Raman From Background Fluorescence Signal?
-- By Excitation Wavelength, Time Gating, and Data Processing

- Substances to Be Studied:
-- BTEX, PCE, TCE, DCE, Carbon Tetrachloride, Chloroform, Hexane, Cyclohexane

Fiber Optic Raman Sensors (cont.)

<u>Tasks</u>

(1) Characterizing Fibers
- **Attenuation versus Wavelength**
- **Interferences**
- **Fiber Transmission Times**

(2) Design Decision on Detector
- **PMT vs. CCD**

(3) Characterizing Wavelength Dependence of the Resonance Enhancement
- **Determine Optimum Wavelengths**

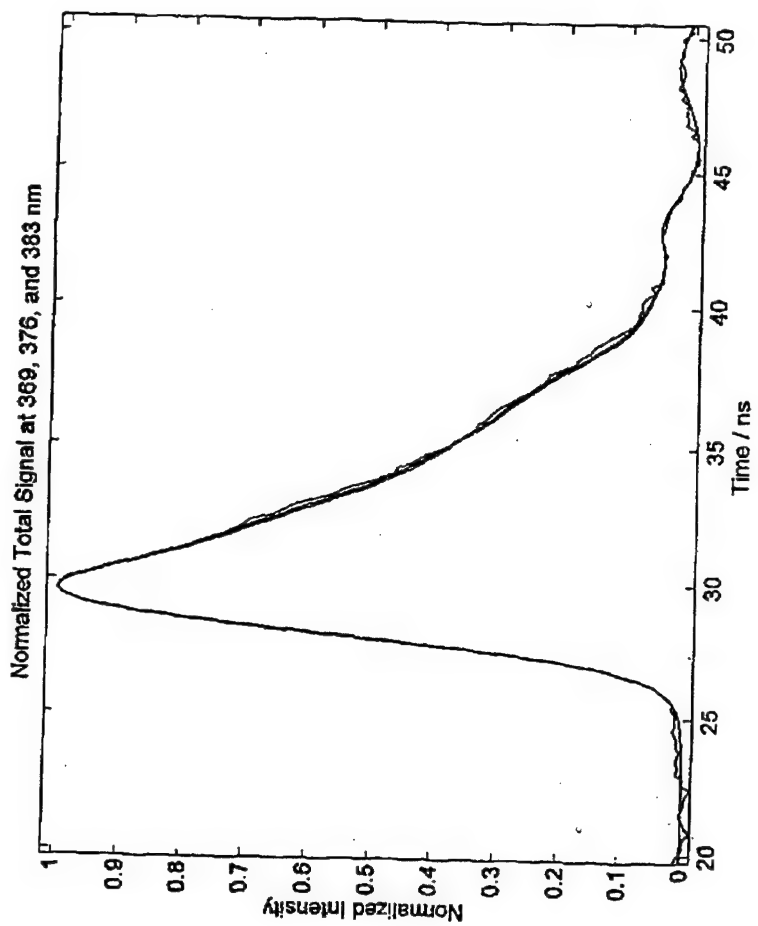
Fiber Optic Raman Sensors (cont.)

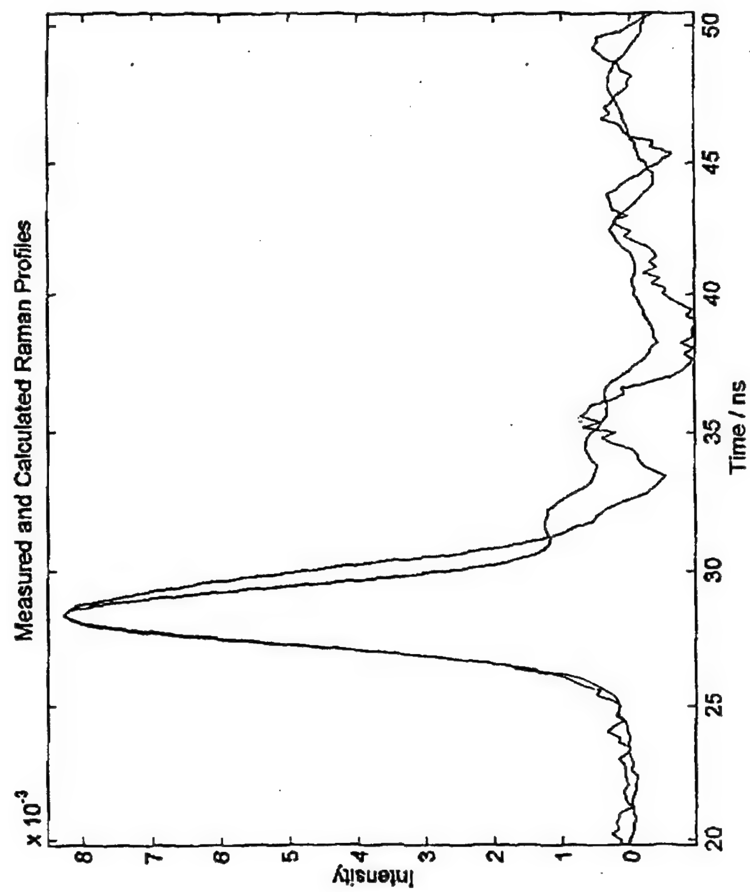
Tasks

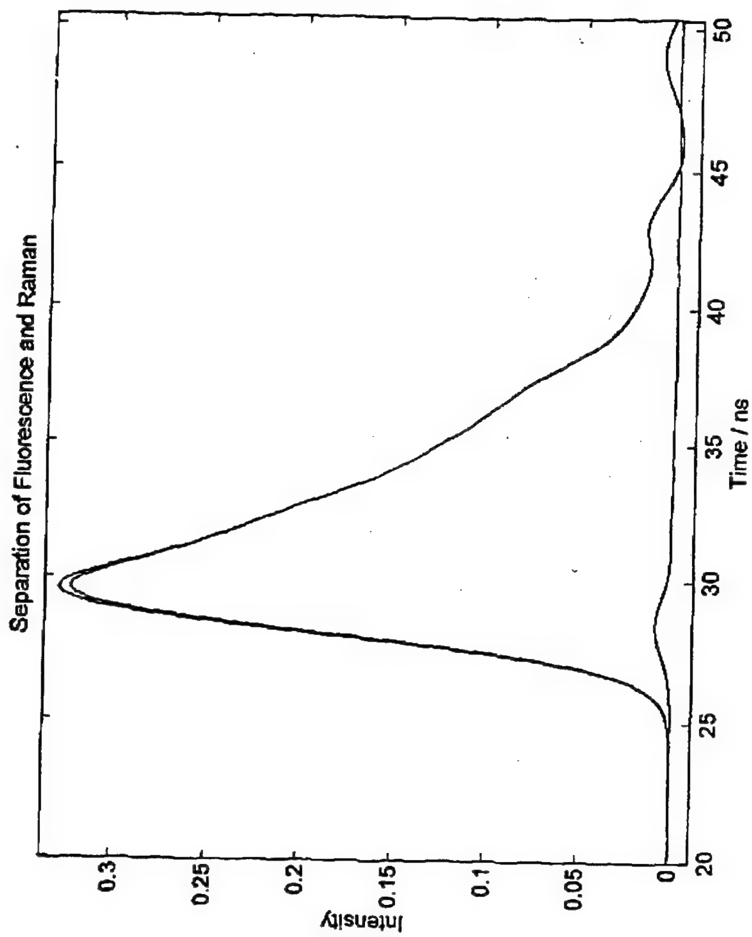
(4) Suppressing Background Fluorescence With Time Shifting
- Time Resolved Raman for Fluorescence Suppression
  -- The Raman Signal Is Coincident With the Laser Pulse

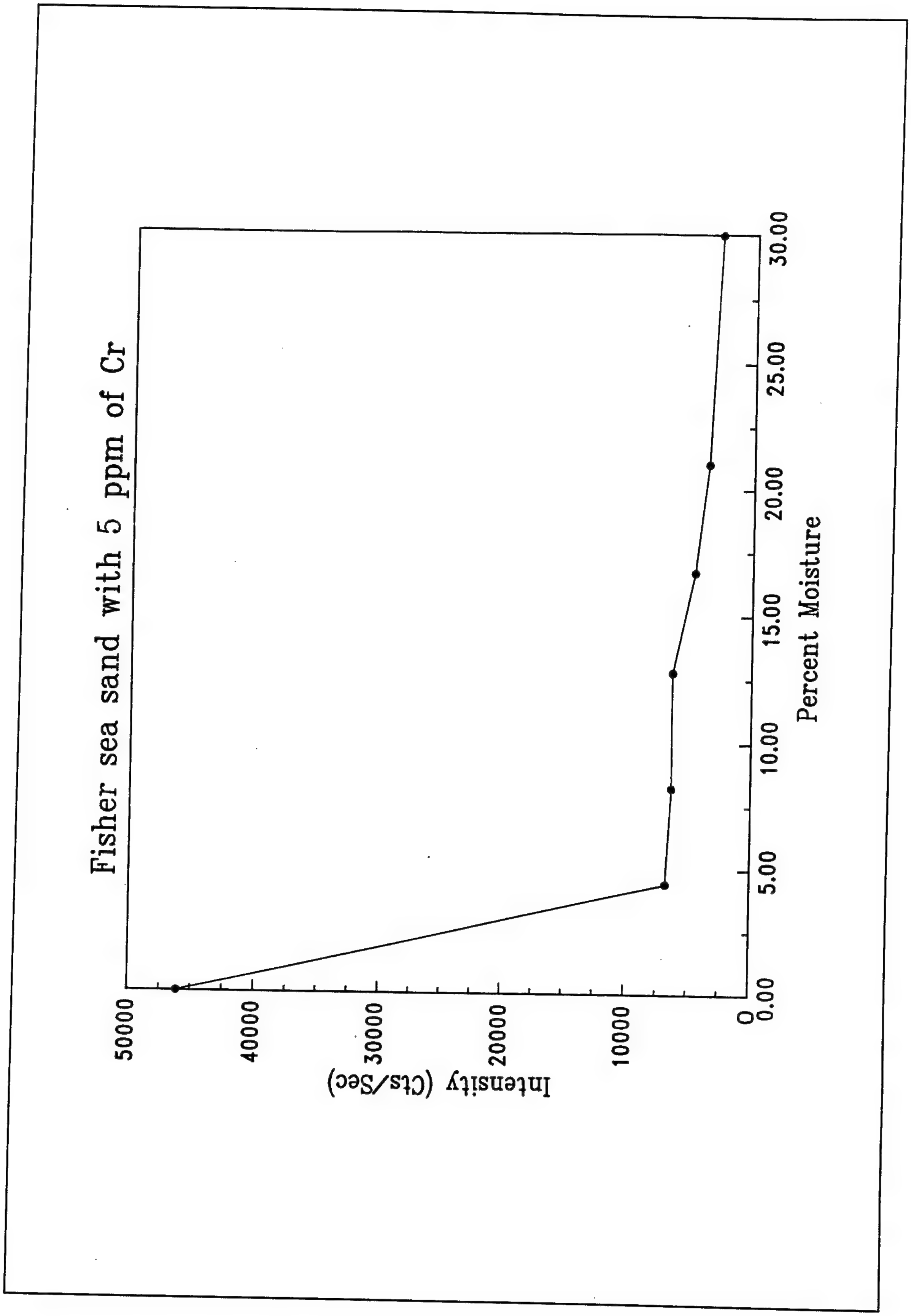
(5) Wavelength Shifting of the Raman Excitation Source
- For Fluorescence Suppresion

(6) Development of Data Analysis Methods For Real-Time Processing of Raman Spectral Data


Normalized Total Signal at 369, 376, and 383 nm
Normalized Intensity
Time / ns
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
20
25
30
35
40
45
50


Measured and Calculated Raman Profiles
x 10^-3
Intensity
Time / ns
0
1
2
3
4
5
6
7
8
20
25
30
35
40
45
50


Separation of Fluorescence and Raman
Intensity
Time / ns
0
0.05
0.1
0.15
0.2
0.25
0.3
20
25
30
35
40
45
50


Fisher sea sand with 5 ppm of Cr
Intensity (Cts/Sec)
50000
40000
30000
20000
10000
0
Percent Moisture
0.00
5.00
10.00
15.00
20.00
25.00
30.00

RESEARCH AREA IV ELECTROCHEMICAL SENSOR

Milestones

Milestone	Schd	Reschd	Comp
• Complete fabrication of prototype VOC and explosives sensors	10/94	09/94	09/94
• Complete initial field test of first generation TNT sensors	10/94	09/94	09/94
• Complete demonstration of improved electrochemical sensor systems	01/96		

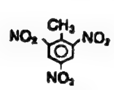
TECHNICAL DESCRIPTION

- **SCAPS probe prototype that incorporates:**
  - External heater to desorb and pyrolyze explosives contaminants in soils
  - Pneumatic system to transport pyrolysis vapors to internal sensors
  - Electrochemical sensor to detect vapors (selective to NO)
  - Signal conditioning electronics
  - Geophysical sensors (sleeve friction and tip resistance)
  - Grouting capability

- **Probe collects soil classification data (site stratigraphy) continuously during push**
- **Probe collects contaminant data during retraction at discrete locations (approx. 1 minute required for each analysis)**

ELECTROCHEMICAL SENSORS FOR SCAPS

- **Low cost**
- **Small size**
- **Simple circuit requirements**
- **Low power requirements**
- **Powerful analytical properties**

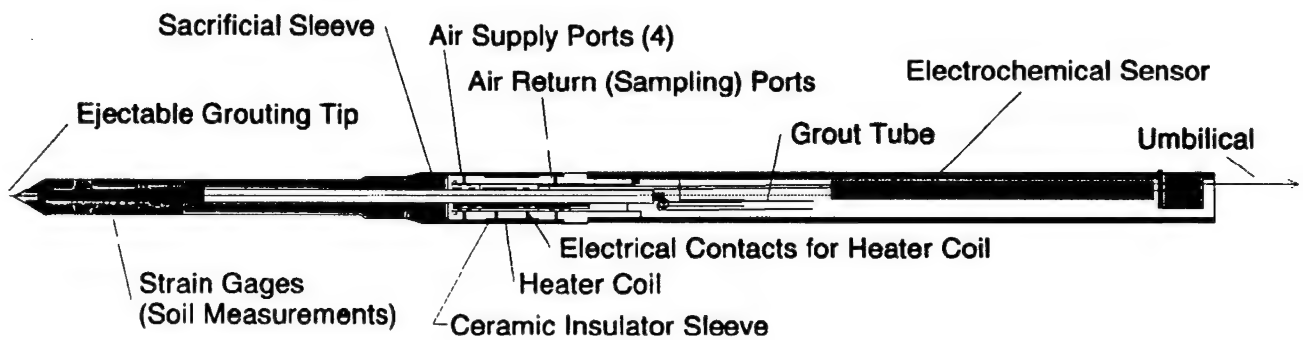


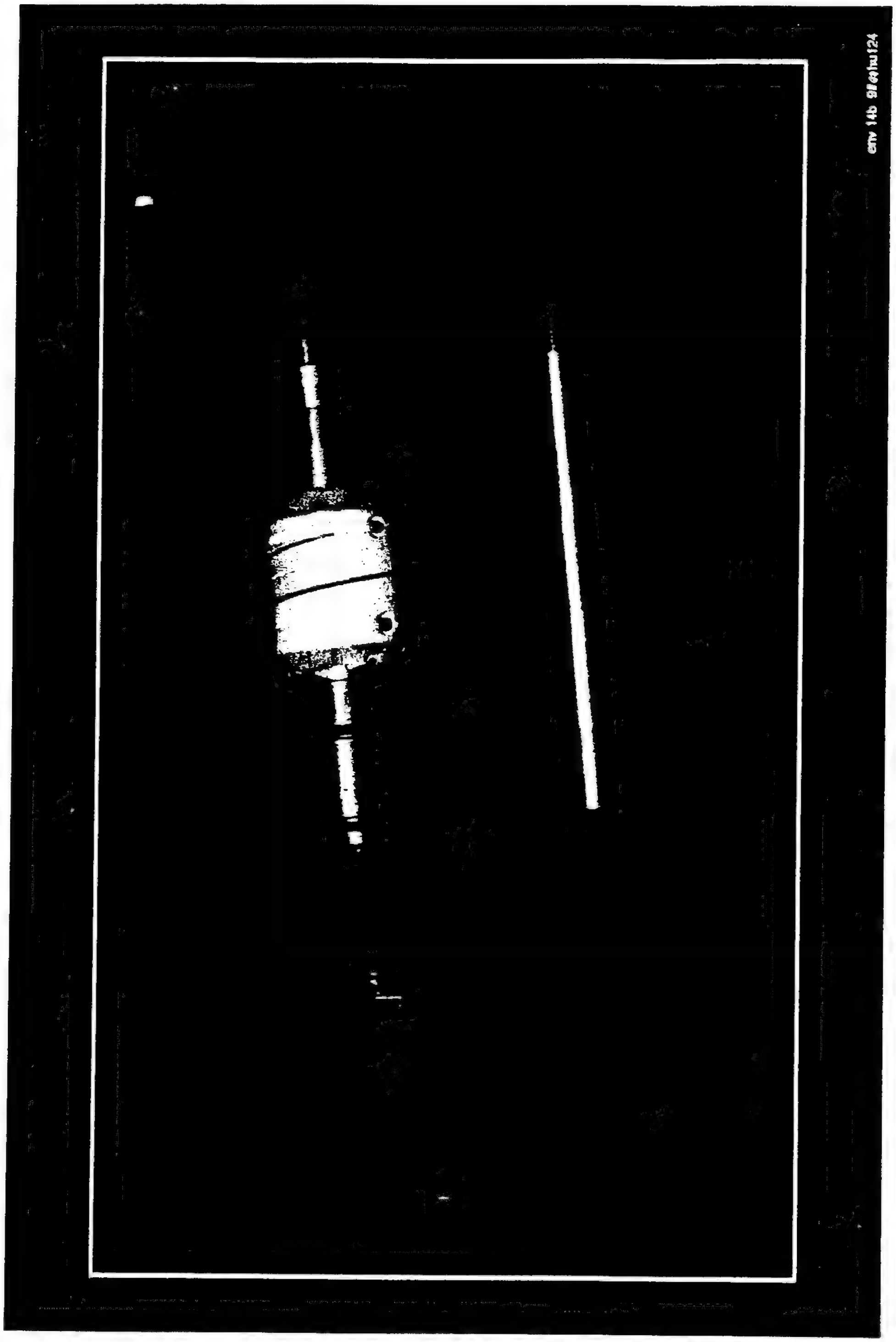
$$+ O_2 \xrightarrow[\Delta]{900°C} CO_2 + H_2O + CO + NO + NO_2$$

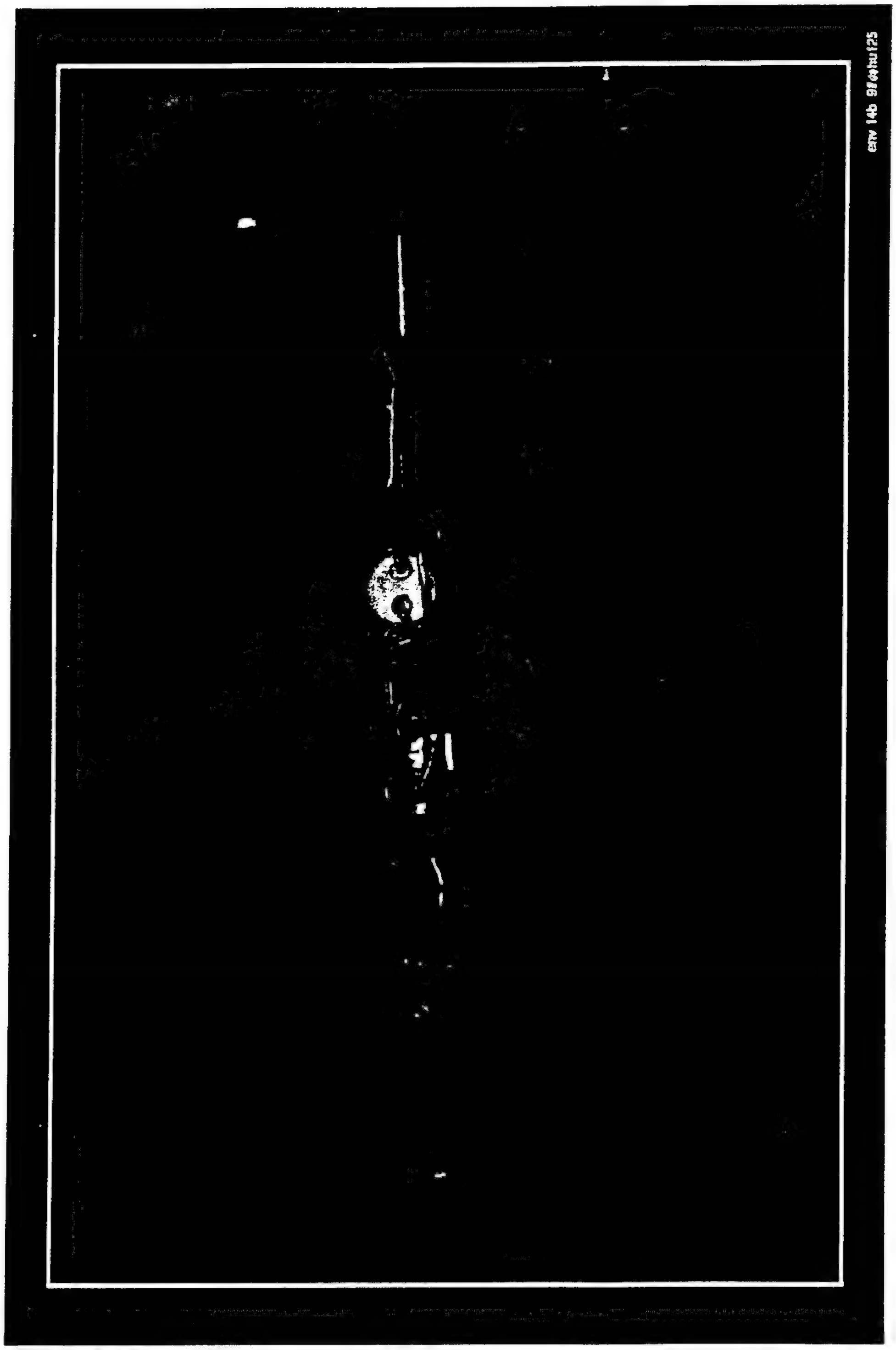
$$NO + H_2O \rightleftharpoons NO_2 + 2H^+ + 2e^-$$

SERDP
Strategic Environmental Research and Development Program
A Partnership to Improve the Environment

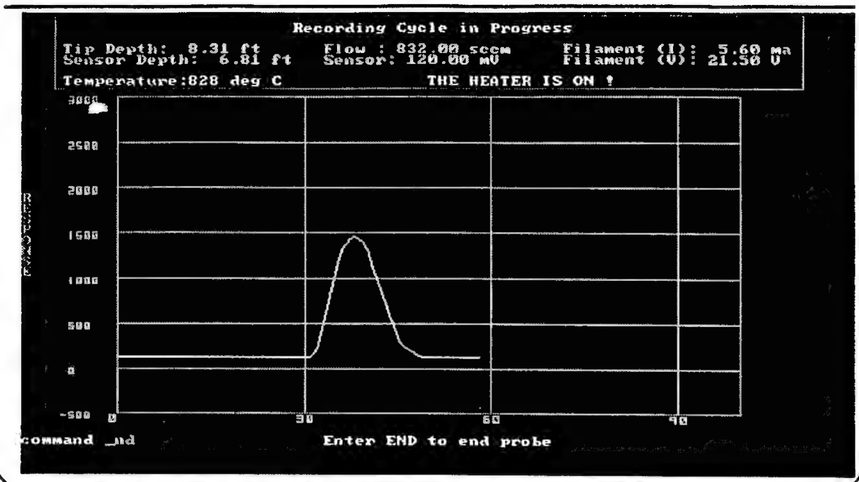
Schematic Of SCAPS Probe For Explosive And Geophysical Sensors





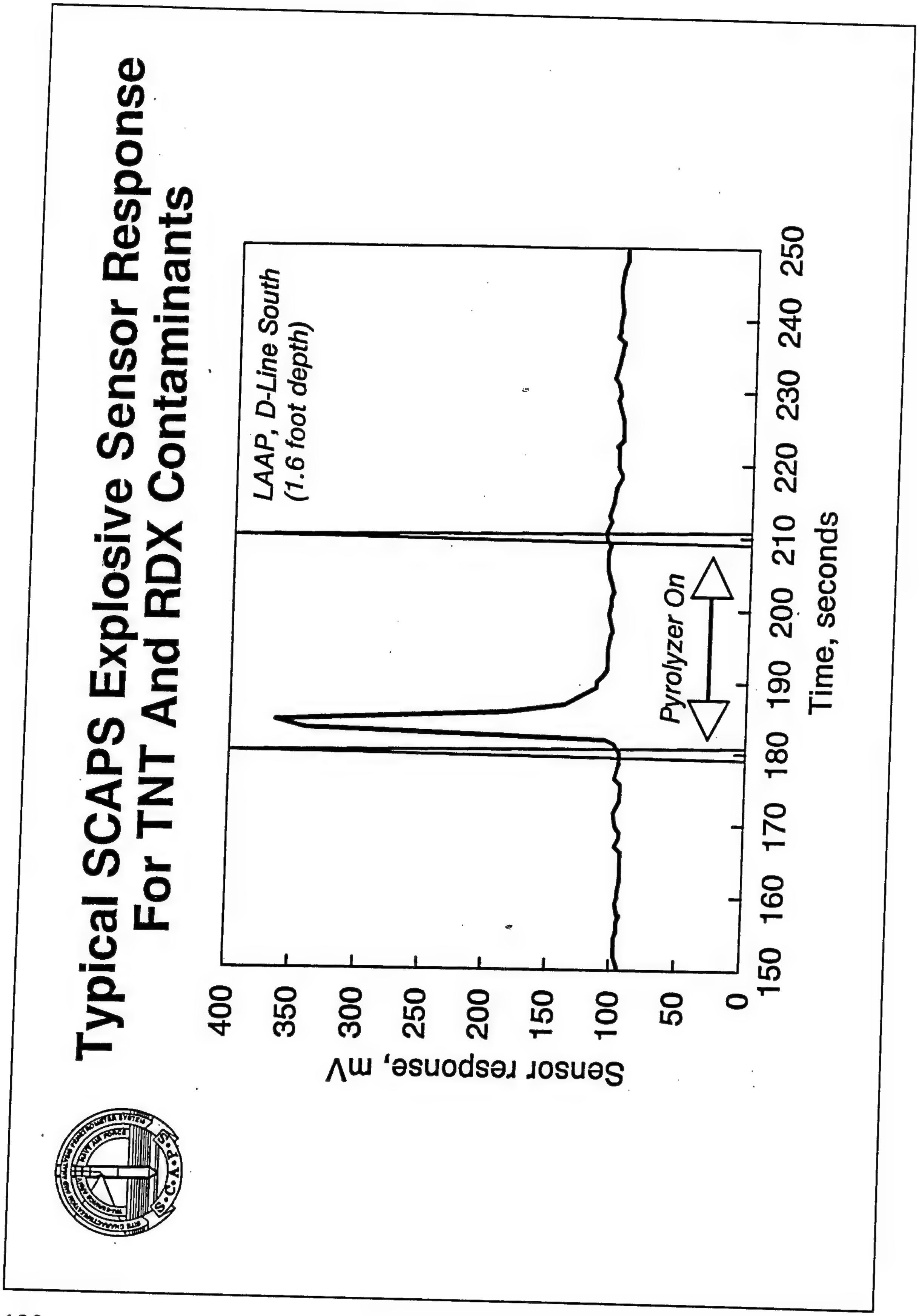


DATA ACQUISITION DISPLAY

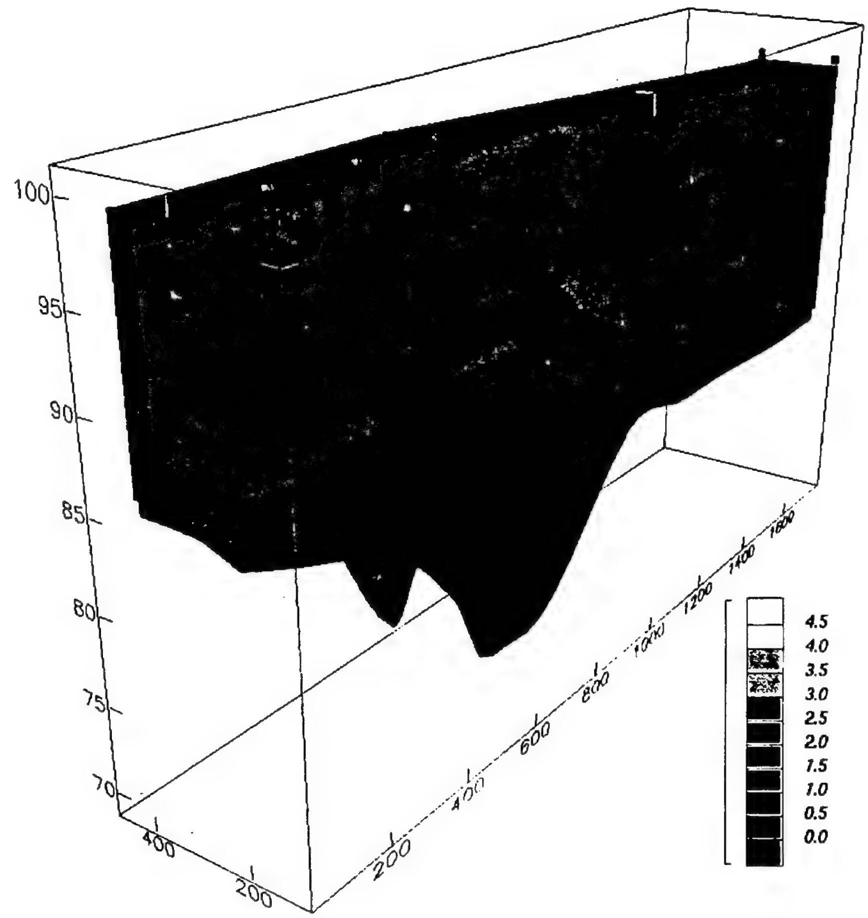


FIELD TESTS

- **Louisiana Army Ammunition Plant, LA, 12-16 Sep 1994**
  - First prototype tested
  - Heterogeneous TNT/RDX contamination
  - Wet clay conditions
  - Improvements identified
- **Pantex, TX (DOE), 6-10 Mar 1995**
  - Modified probe tested
  - Dry sand / clay conditions
  - Heterogeneous RDX / HMX contamination
- **Volunteer Army Ammunition Plant, TN, 3-7 Apr 1995**
  - Improved pneumatic system
  - Improved data acquisition / display system
  - Moist clay conditions
  - Homogeneous (near surface) TNT contamination


Typical SCAPS Explosive Sensor Response
For TNT And RDX Contaminants
LAAP, D-Line South
(1.6 foot depth)
Pyrolyzer On
Sensor response, mV
400
350
300
250
200
150
100
50
0
150
160
170
180
190
200
210
220
230
240
250
Time, seconds
S.C.A.P.S.

Pantex
Soil Stratigraphy

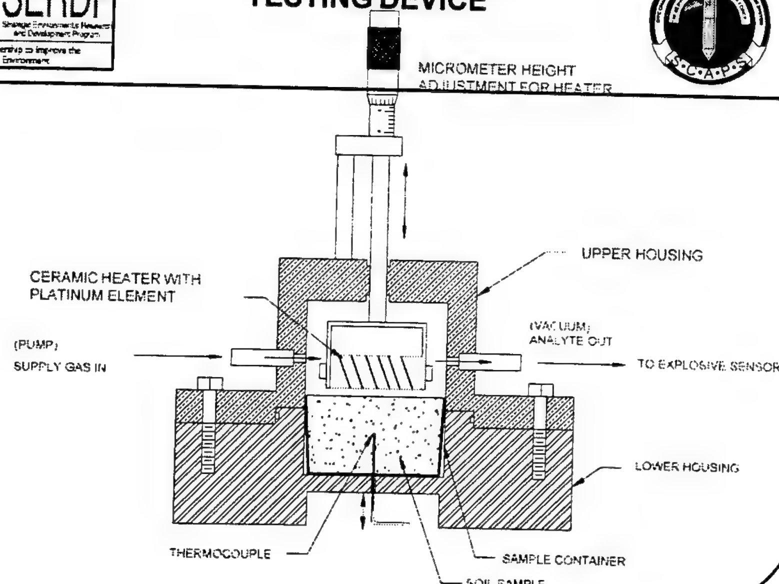


VOLUNTEER ARMY AMMUNITION PLANT TEST 03-06 APRIL 1995

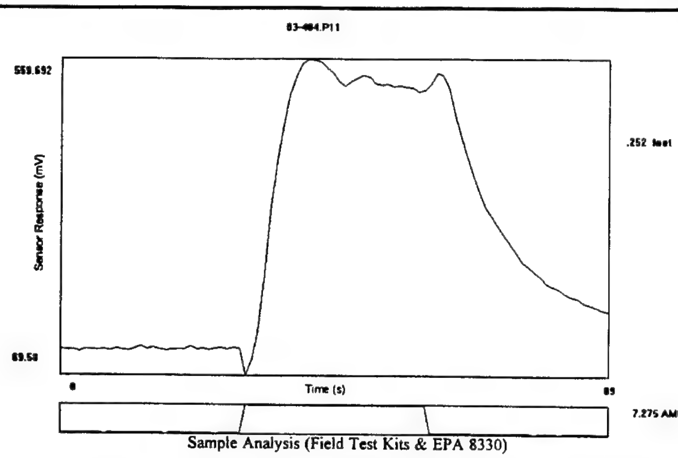
Sample Name	Location	Depth (ft BGS)	SCAPS Sensor Response (mV)	Field Screen TNT (mg/kg)	EPA 8330 TNT (mg/kg)	EPA 8330 2,4DNT (mg/kg)
SS9	App. 1.5 ft N of 09-405	7.9-8.1	60	<0.7	0.3	<0.25
SS1	App. 3ft E of 06-404	0-0.33	69	0.7	0.4	<0.25
SS6	App. 0.5 ft E of 04-404	0-0.25	156.7	12.1	3.6	<0.25
SS13	App. 0.66ft W of 12-504	0-0.3	363.5	6.8	NP	NP
SS4	App. 0.66 ft S of 03-404	0.17-0.33	488	3.8	NP	NP
SS3	App. 0.33ft W of 03-404	0-0.2	590.5	377.5	413	2.1
SS10	Between 07&08-404/5	0-0.2	811	89.1	4	<0.25
SS11	Between 07&08-404/5	0.25-0.40	1132	756	NP	NP
SS12	Between 07&08-404/5	0.5-0.6	SAT.	601	105000	57.5

Note: NP indicates that the sample was not analyzed in the laboratory by EPA method 8330. SAT. indicates that the sensor reached saturation (3142 mV).

LABORATORY EXPLOSIVES SENSOR TESTING DEVICE



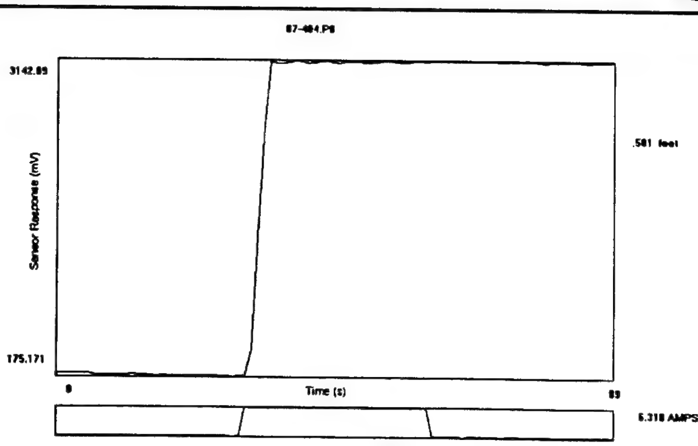
SCAPS EXPLOSIVES SENSOR RESPONSE (VAAP Test 03-06 Apr 1995)



Sample Analysis (Field Test Kits & EPA 8330)

3.8 ppm	0.17-0.33 ft depth	0.66 ft West of SCAPS push
413 ppm	0.0-0.2 ft depth	0.33 ft West of SCAPS push

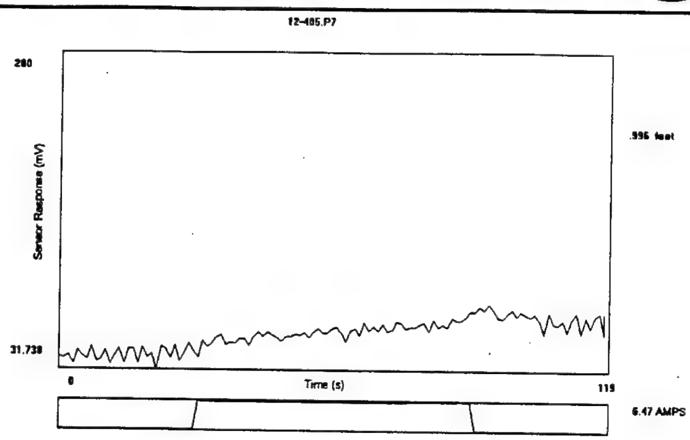
SCAPS EXPLOSIVES SENSOR RESPONSE (VAAP Test 03-06 Apr 1995)



Sample Analysis (EPA 8330)

10.5% TNT 0.5-0.6 ft Depth 2 ft South of SCAPS push

SCAPS EXPLOSIVES SENSOR RESPONSE (VAAP Test 03-06 Apr 1995)



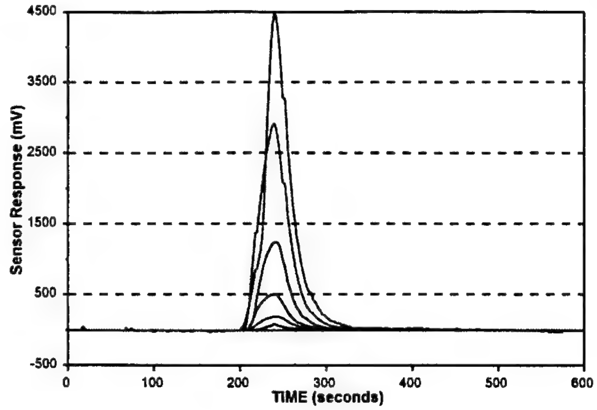
Sample Analysis (Field Test Kit & EPA 8330)

<0.7 ppm   1.0 - 1.5   0.66 ft W of SCAPS push

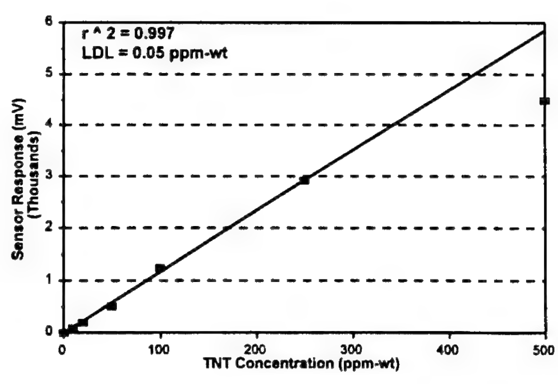
EXPLOSIVES SENSOR DEVELOPMENT AND TESTING

- **Accomplishments**
  - Conducted extensive laboratory testing of electrochemical sensors
  - Completed three SCAPS field tests at explosives contaminated sites
- **Planned**
  - Complete laboratory characterization of pyrolysis products
  - Scheduled to conduct additional field tests at Longhorn Army Ammunition Plant, TX during Sep 95 and Camp Navajo, AZ during Oct 95
  - Field tests / demos at VAAP during 1996

CALIBRATION OF THE EXPLOSIVES SENSOR 10, 20, 50, 100, 250, 500 ppm-wt TNT



CALIBRATION OF EXPLOSIVES SENSOR



SCAPS ELECTROCHEMICAL VOC SENSOR

William M. Davis

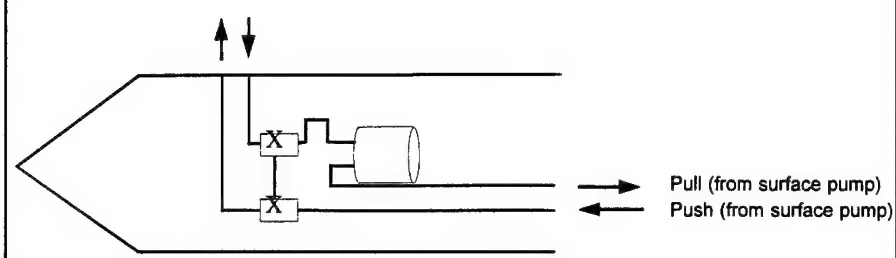
Waterways Experiment Station

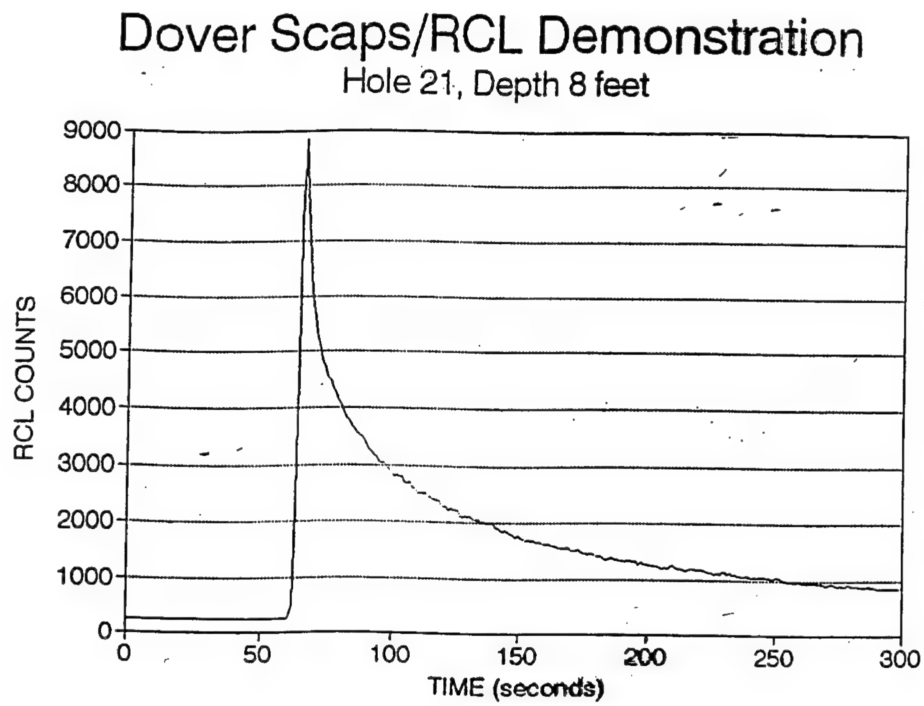
SCAPS Electrochemical VOC Sensor

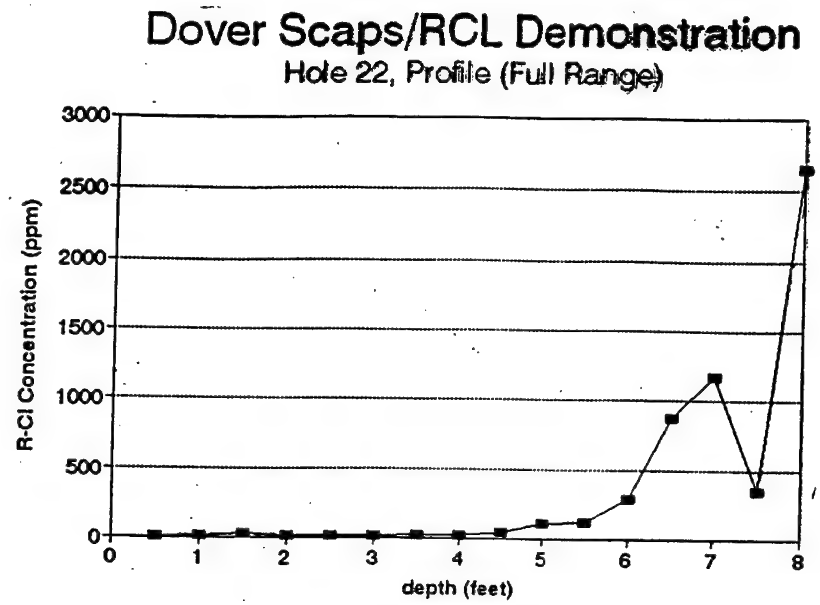
- Based on Chlorine selective RCI sensor developed by Transducer Research, Inc.
- Plans to incorporate non-chlorinated VOC Sensor
- Soil vapor sensor, deployed in the probe housing designed for the Electrochemical Explosives sensor
- Field tested at Dover AFB, DE in May 1995

SCAPS Electrochemical VOC Sensor

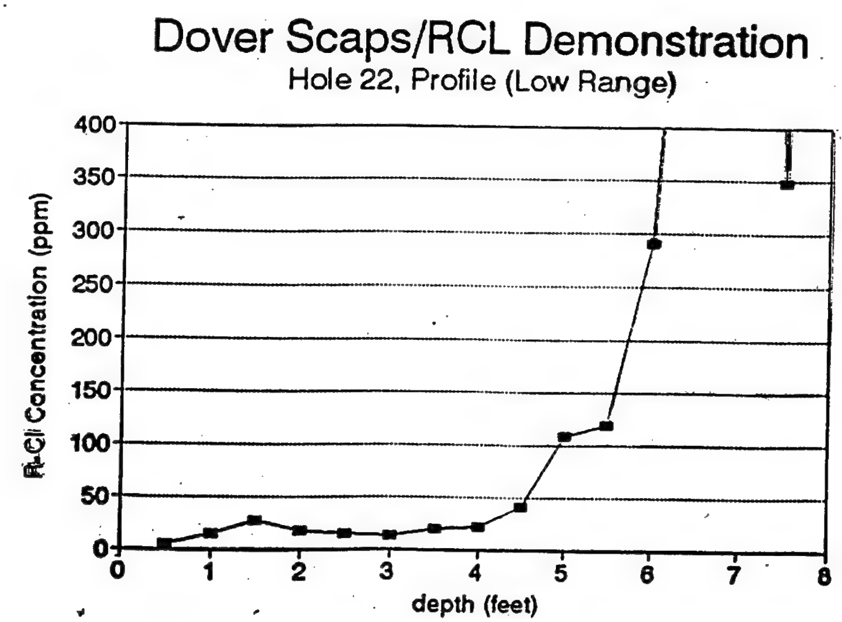
(SCHEMATIC DIAGRAM)




Dover Scaps/RCL Demonstration
Hole 21, Depth 8 feet
RCL COUNTS
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
50
100
150
200
250
300
TIME (seconds)



Dover Scaps/RCL Demonstration
Hole 22, Profile (Full Range)
R-Cl Concentration (ppm)
3000
2500
2000
1500
1000
500
0
0
1
2
3
4
5
6
7
8
depth (feet)



Dover Scaps/RCL Demonstration
Hole 22, Profile (Low Range)
R-Cl Concentration (ppm)
400
350
300
250
200
150
100
50
0
0
1
2
3
4
5
6
7
8
depth (feet)

SCAPS Electrochemical VOC Sensor

- Successfully field tested the RCI sensor alone
- Modify current probe design to include non-chlorinated VOC sensor
- Perform additional field test

SCAPS Electrochemical VOC Sensor

- Performers:
  - WES: William M. Davis
    Ernesto Cespedes
  - TRI: William Buttner
    Mel Findley

RESEARCH AREA V SPECTRAL GAMMA PROBE

Milestones	Schd	Reschd	Comp
• Complete improved SCAPS spectral gamma probe	03/95	10/95	
• Complete field testing / demonstration of improved gamma probe	02/96		

Spectral Gamma Probe Participants

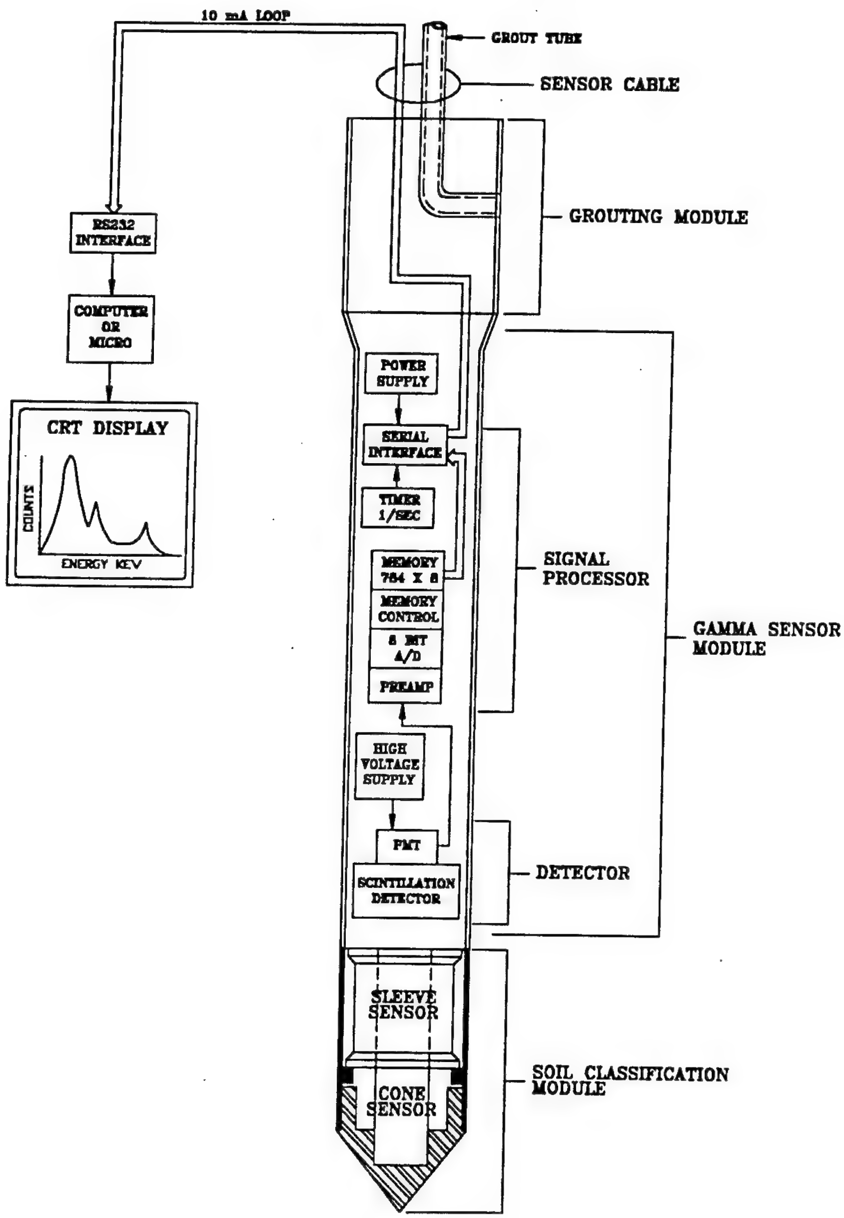
Principal Investigator: Ernesto R. Cespedes

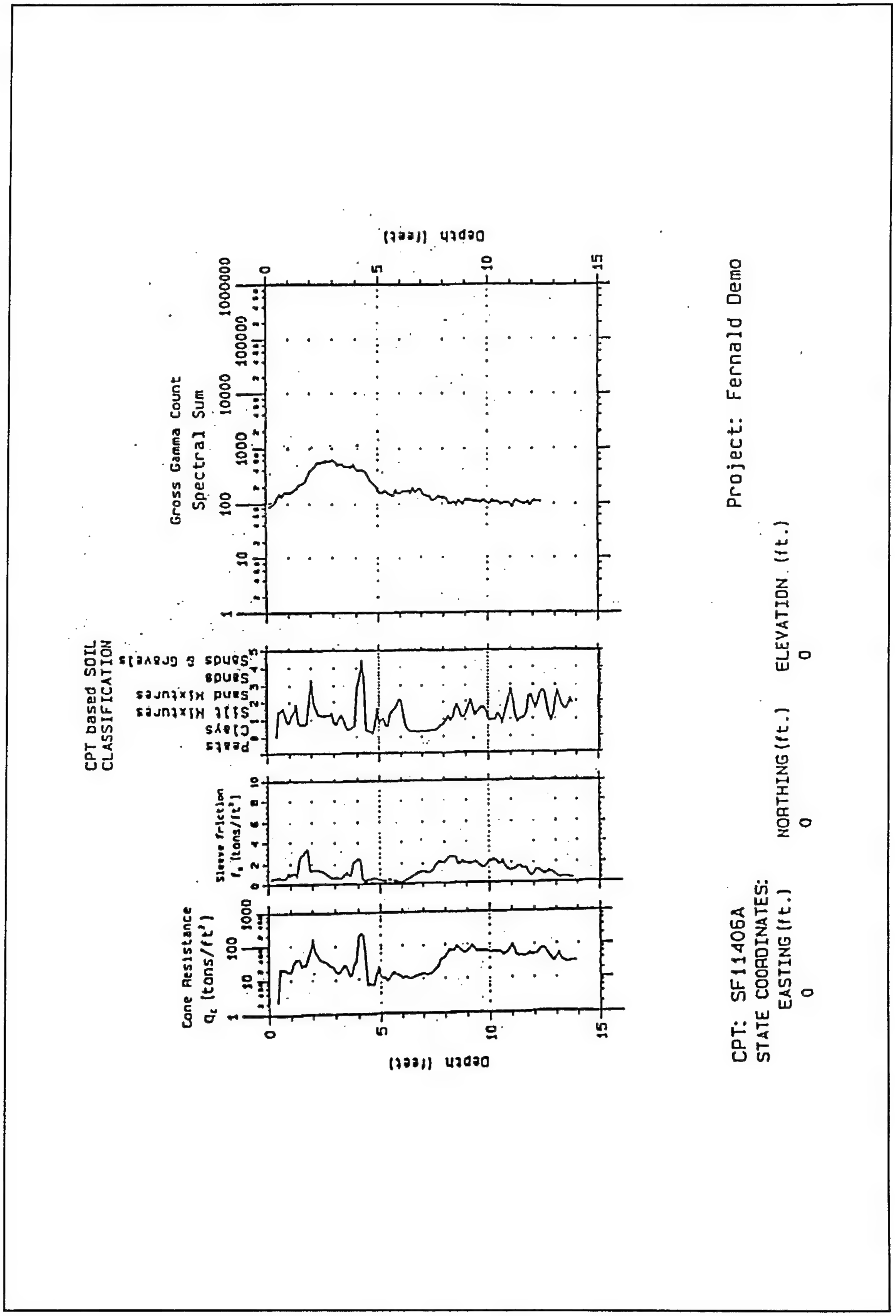
Physicist: Bobby E. Reed

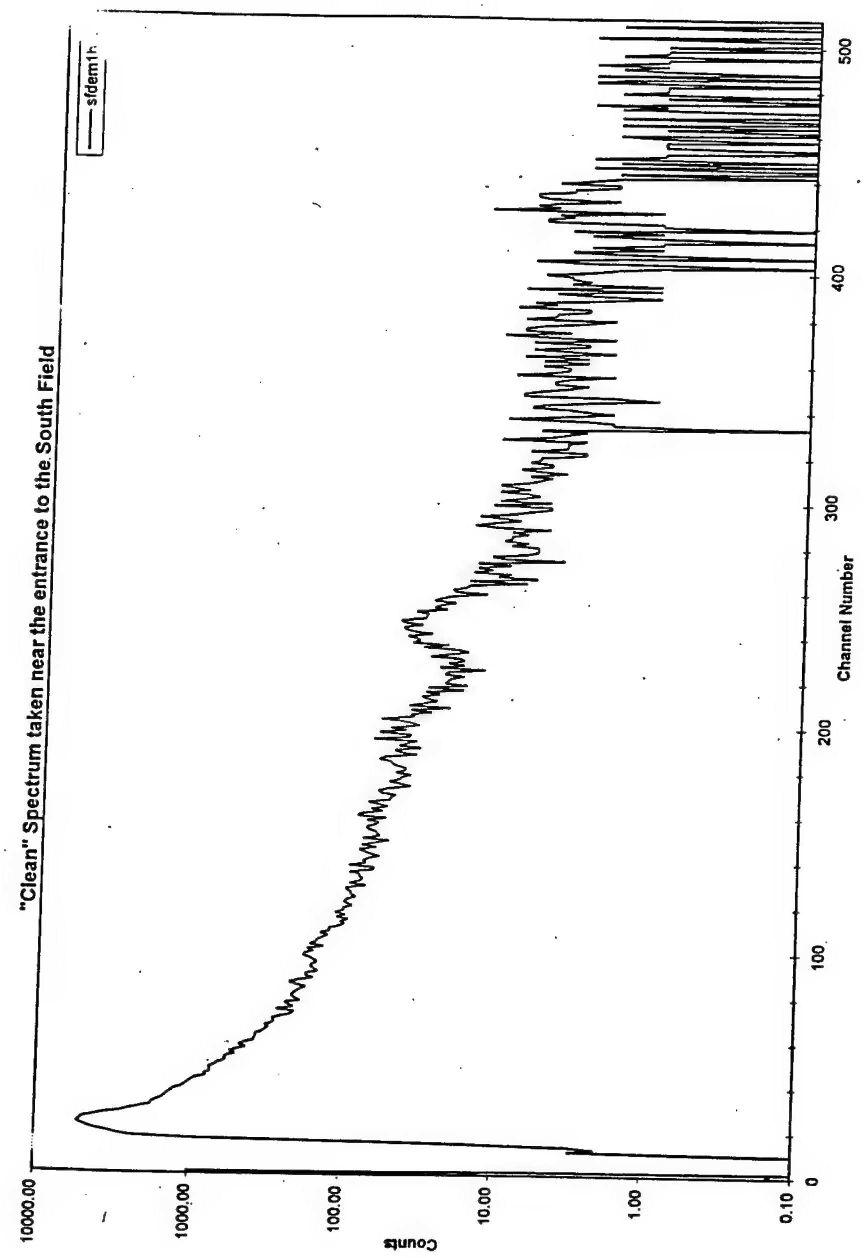
Electrical Engineer: Bryan A. Register

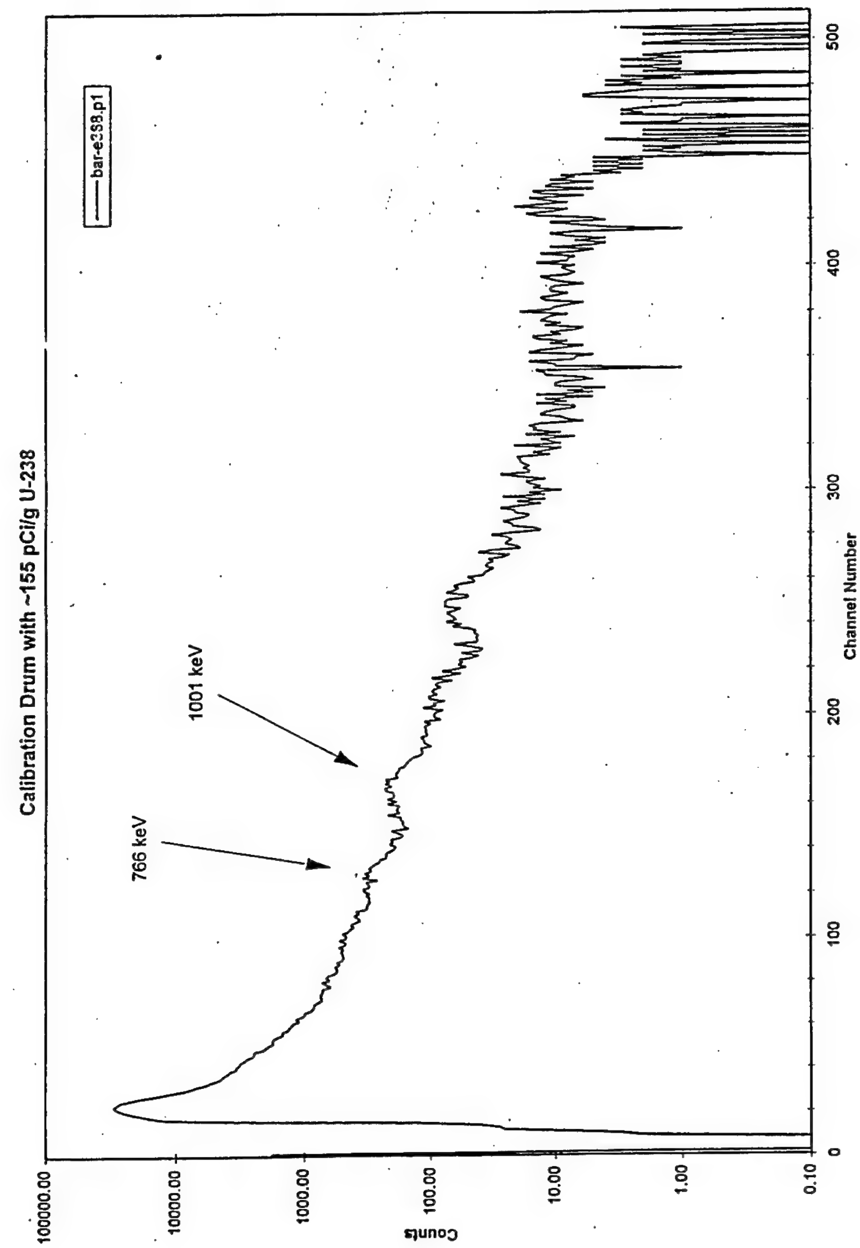
Physicist: John C. Morgan

SPECTRAL GAMMA PROBE DIAGRAM




Cone Resistance
q_c (tons/ft²)
Sleeve friction
f_s (tons/ft²)
CPT based SOIL
CLASSIFICATION
Peats
Clays
Silt Mixtures
Sand Mixtures
Sands
Sands & Gravels
Gross Gamma Count
Spectral Sum
Depth (feet)
Depth (feet)
CPT: SF11406A
STATE COORDINATES:
EASTING (ft.)
0
NORTHING (ft.)
0
ELEVATION (ft.)
0
Project: Fernald Demo


"Clean" Spectrum taken near the entrance to the South Field
sfdem1h
Counts
10000.00
1000.00
100.00
10.00
1.00
0.10
Channel Number
0
100
200
300
400
500


Calibration Drum with ~155 pCi/g U-238
bar-e238.p1
1001 keV
766 keV
Counts
100000.00
10000.00
1000.00
100.00
10.00
1.00
0.10
0
100
200
300
400
500
Channel Number

Spectral Gamma Probe Problems Encountered

Temperature Stability

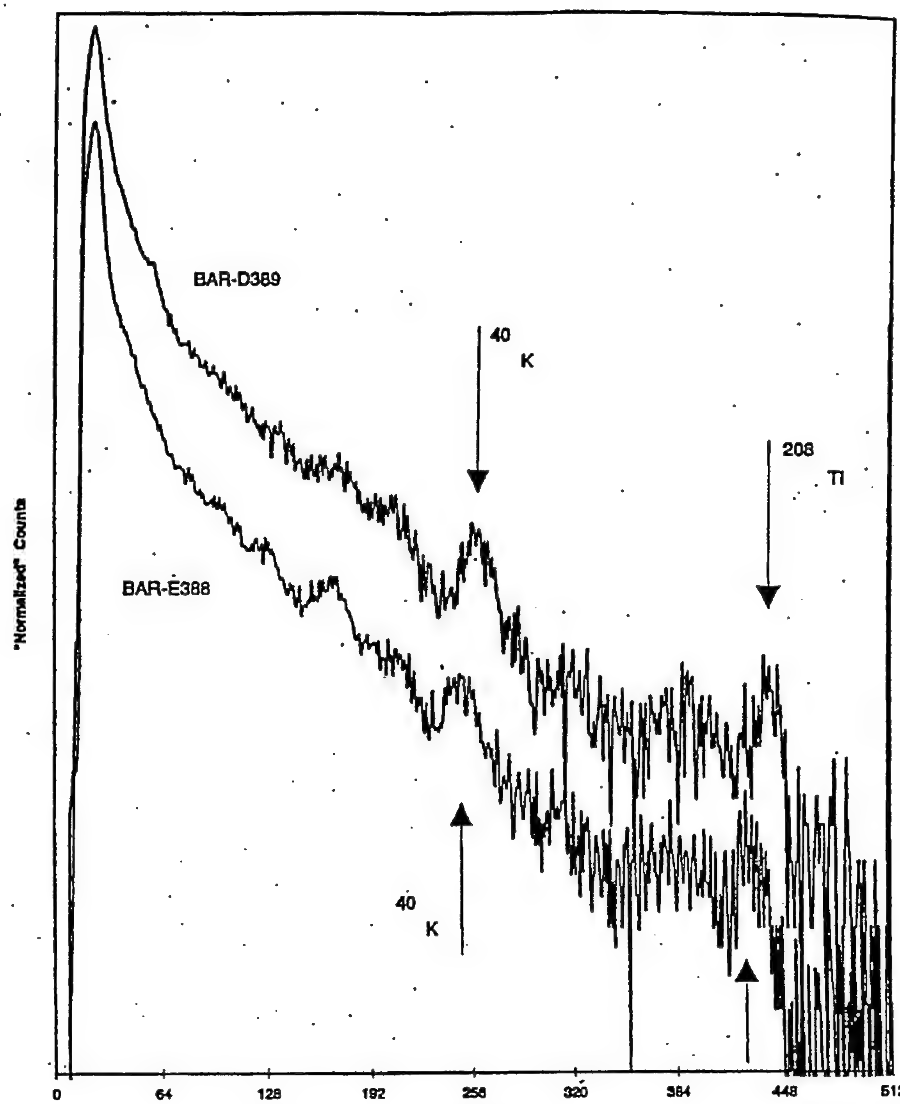
Analysis Difficulty

Housing Attenuation

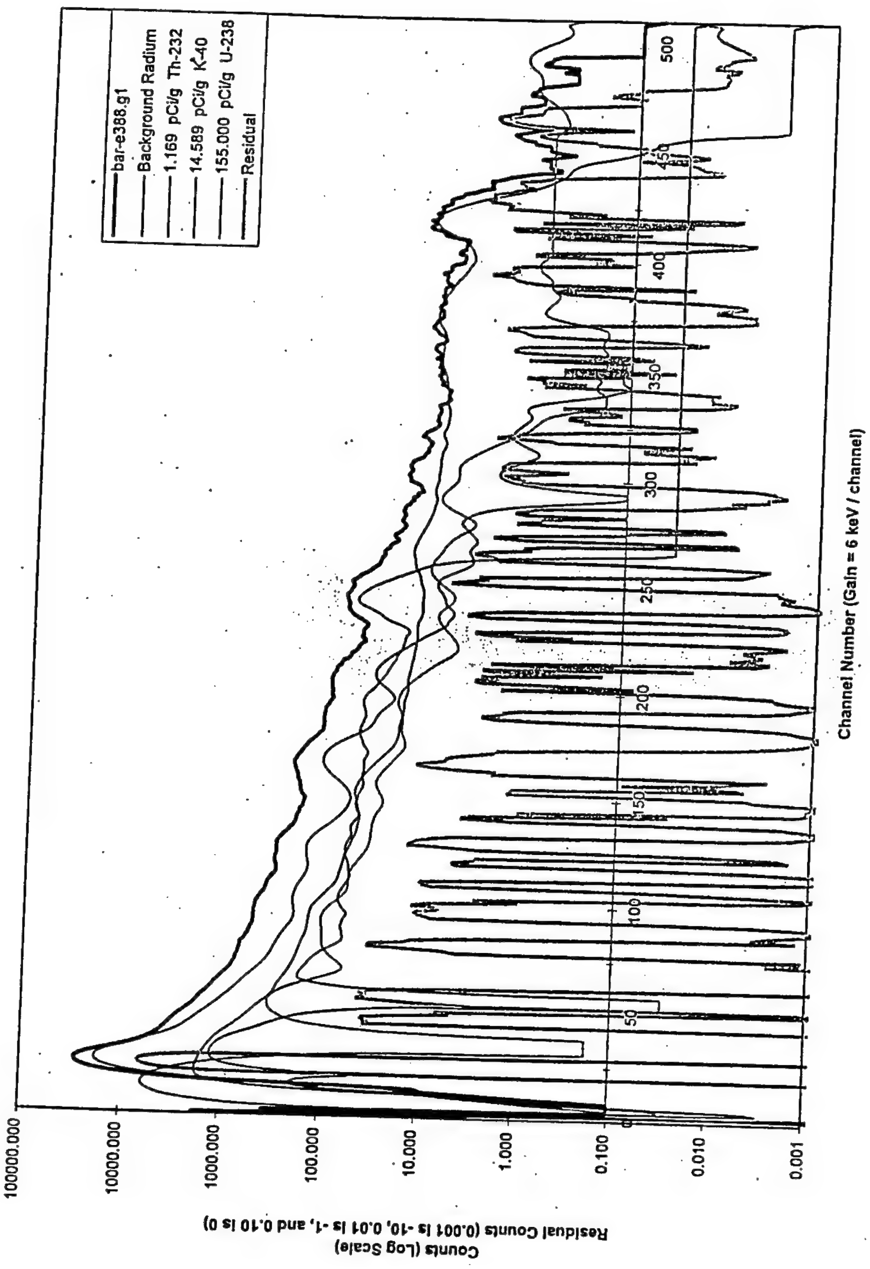
Spectral Gamma Probe Analysis Difficulties Encountered

High Thorium Background

Gain Shifts



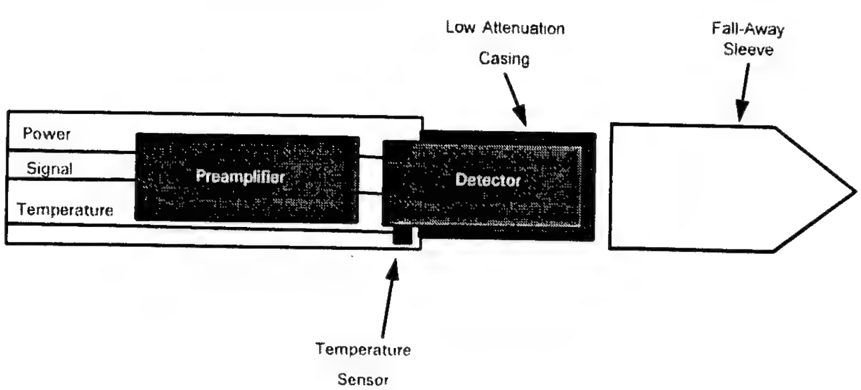
Zero/Gain Shift between the BAR-D389 and BAR-E388 Spectra


bar-e388.g1
Background Radium
1.169 pCi/g Th-232
14.589 pCi/g K-40
155.000 pCi/g U-238
Residual
100000.000
10000.000
1000.000
100.000
10.000
1.000
0.100
0.010
0.001
Counts (Log Scale)
Residual Counts (0.001 is -10, 0.01 is -1, and 0.10 is 0)
50
100
150
200
250
300
350
400
450
500
Channel Number (Gain = 6 keV / channel)

Spectral Gamma Probe Improvements

- **Standard Electronics**
  - Custom electronics have been replaced with modular NIM rack mounted industry standards
- **Improved Data Storage**
  - Data is stored in small blocks allowing post processing methods
- **Temperature Correction Algorithms**
  - Gain shift and offset problems from temperature sensitive components can be corrected in post processing
- **Fall-away Sleeve**
  - Allows low energy portions of the spectrum to be observed, and reduces noise from scattered photons

Spectral Gamma Probe Fall-Away Sleeve



RESEARCH AREA VI
SAMPLING TECHNOLOGY

SERDP
Strategic Environmental Research and Development Program
A Partnership to Improve the Environment

S•C•A•P•S

Milestones	Schd	Reschd	Comp
• Complete initial testing of thermal desorption VOC sampler	05/95		05/95
• Complete field evaluations of multiport VOC sampler	06/95		05/95
• Complete laboratory testing of analyte behavior in soils	08/96		
• Complete field tests of thermal desorption VOC sampler interfaced to analytical instr	10/96		
• Complete description of analyte behavior in soils	12/96		
• Complete evaluation of quantitative aspects of SCAPS samplers	12/96		

DoD EPA DOE

SERDP

Strategic Environmental Research and Development Program

A Partnership to Improve the Environment

S·C·A·P·S

SITE CHARACTERIZATION AND ANALYSIS PENETROMETER SYSTEM

TRI-SERVICE ARMY NAVY AIR FORCE

ANALYTE BEHAVIOR IN REGION OF SAMPLER

PROBLEM

- THE RELATIONSHIP BETWEEN SOIL CONTAMINANT CONCENTRATION AND THE CONCENTRATION MEASURED BY THE SAMPLER ARE UNKNOWN

APPROACH

- DEVELOP COMPUTATIONAL PROCEDURES
  VAPOR DRAWDOWN AND CONE OF INFLUENCE
- LABORATORY EVALUATION
  MIGRATION TO SAMPLING PORT
  GRADIENT CAUSED BY SAMPLING
  ACCURACY OF MEASUREMENT
- EVALUATE PROCEDURES DEVELOPED USING FIELD DATA

BENEFIT

MOVE FROM SCREEN TO SEMI-QUANTITATIVE WITH VAPOR SAMPLING DEVICES

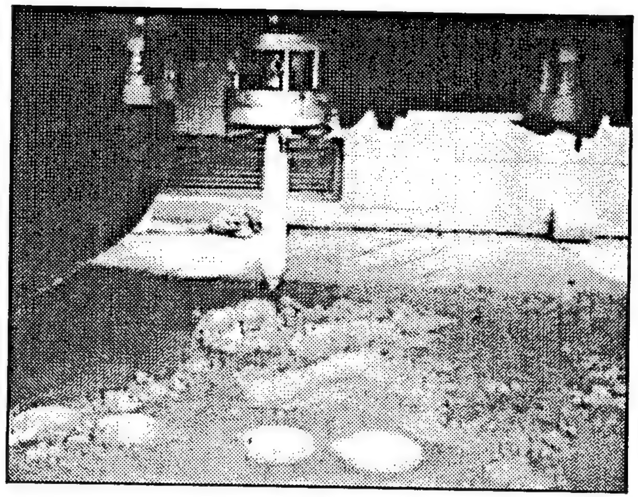
IMPROVED VOC SAMPLER

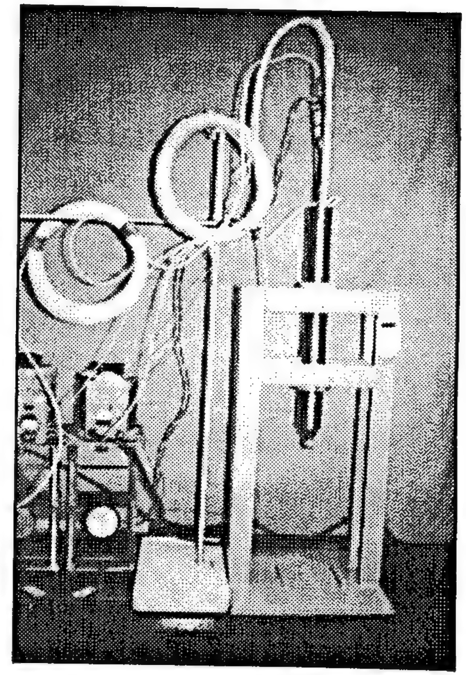
US ARMY ENGINEER WATERWAYS EXPERIMENT STATION

3909 HALLS FERRY ROAD

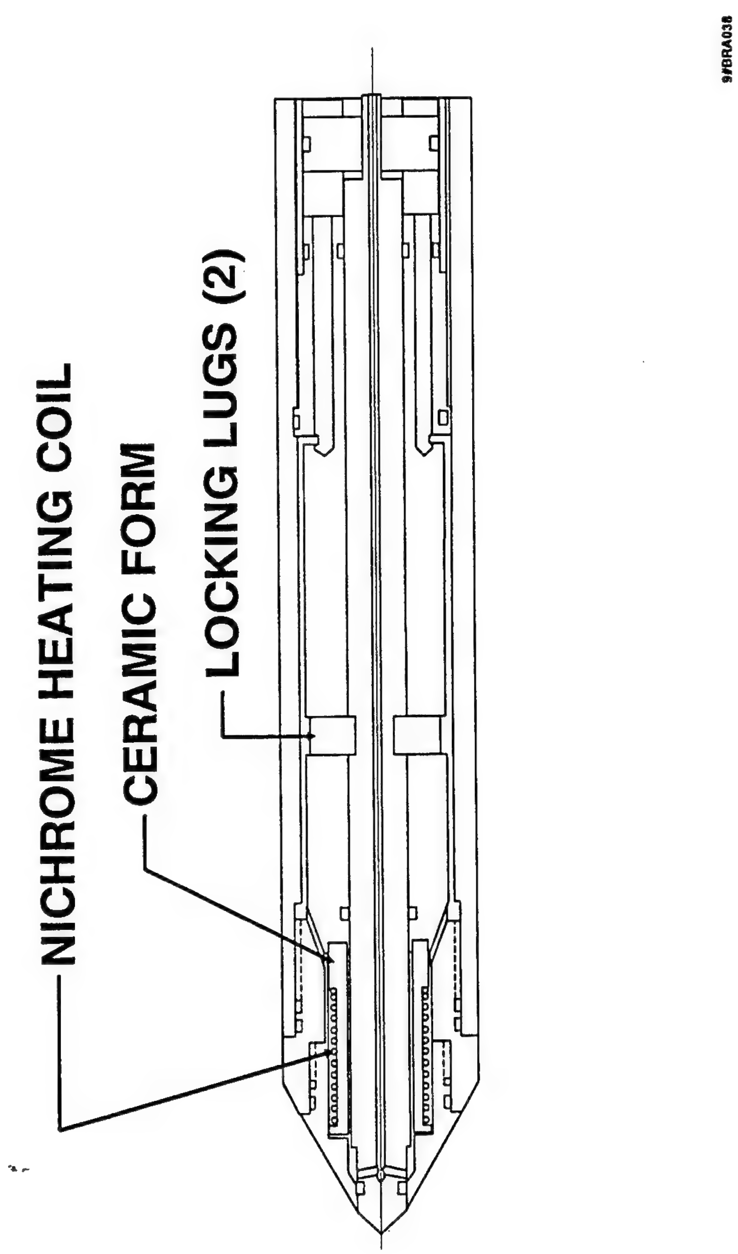
VICKSBURG, MS 39180-6199

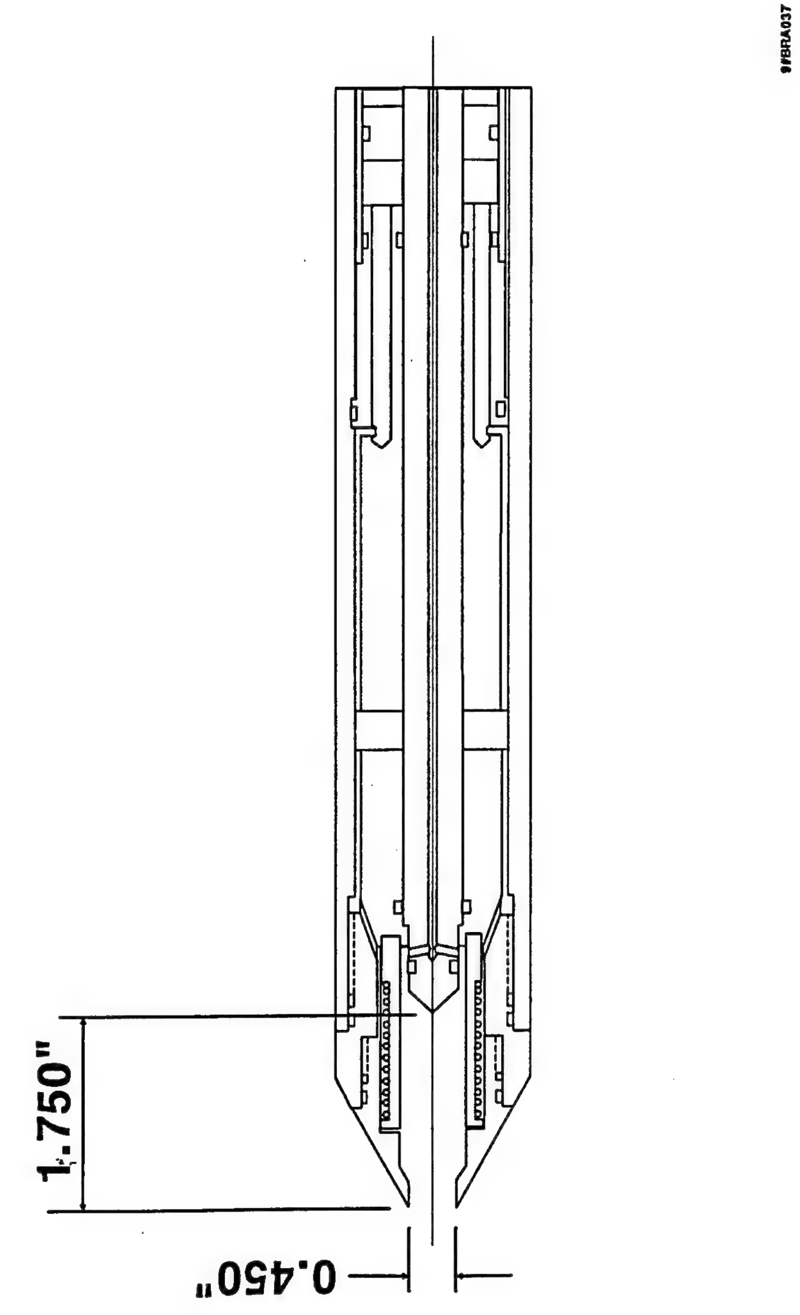
Thermal Desorption VOC Sampler





env 15/b 9f@HU130


NICHROME HEATING COIL
CERAMIC FORM
LOCKING LUGS (2)
9#BRA038


1.750"
0.450"

IMPROVEMENTS

- EXPANDED SUITE OF COMPOUNDS
- SOIL VAPOR SAMPLING
- MECHANICAL SIMPLICITY
- IMPROVED GAS MANIFOLD
- DIRECT ANALYTICAL INTERFACE

APPROACH

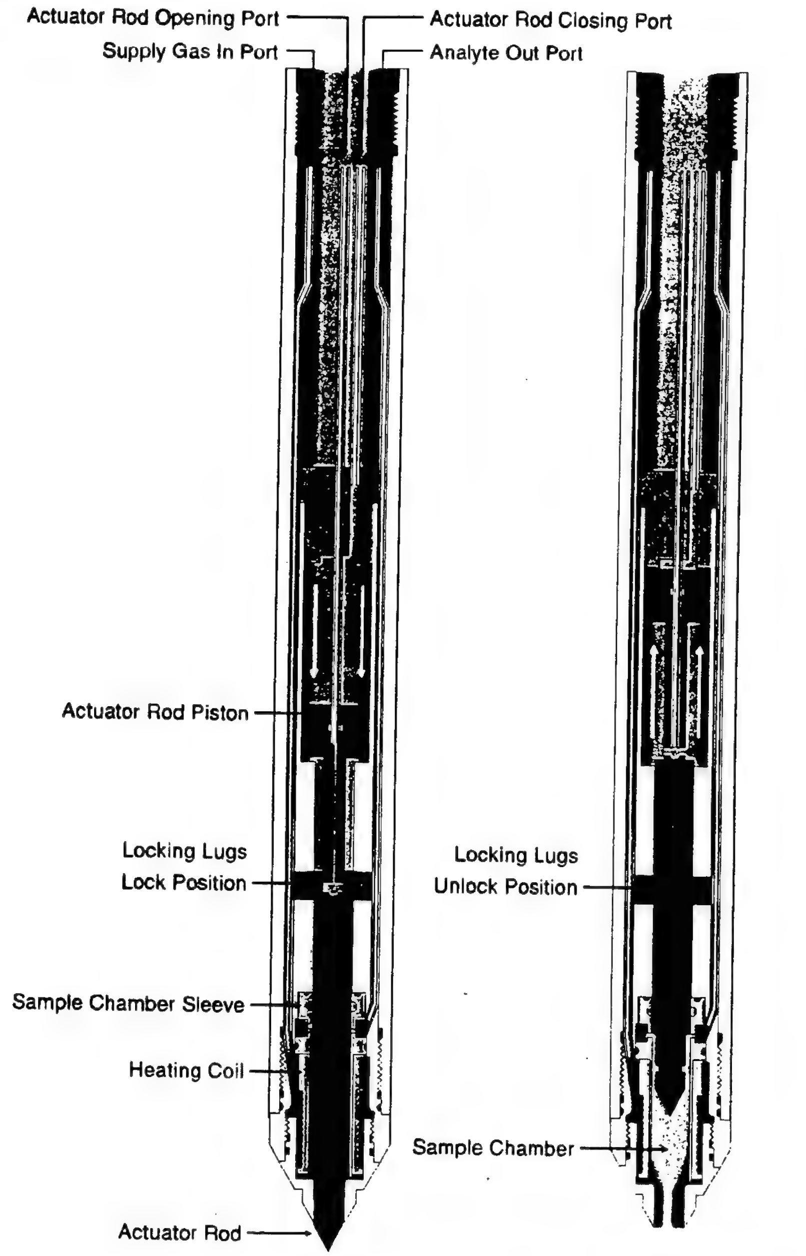
- EXTENDED RANGE OF COMPOUNDS AND PROVIDE FOR DIRECT INSTRUMENT INTERFACE
- EVALUATION OF IMPROVED SAMPLER
- FIELD TEST IN SOIL AND VAPOR SAMPLING MODES
- INTERFACE TO ANALYTICAL INSTRUMENTATION
- FIELD TEST VOC SAMPLER INTERFACED TO ANALYTICAL INSTRUMENTATION

ORIGINAL TARGET COMPOUNDS

trans-1,2-Dichloroethene
Trichloroethene (TCE)
Benzene
Toluene
Chlorobenzene
Ethylbenzene
meta-Xylene
para-Xylene
ortho-Xylene
meta-Dichlorobenzene
para-Dichlorobenzene
ortho-Dichlorobenzene

ADDED COMPOUNDS

1,1-Dichloroethene
cis-1,2-Dichloroethene
Tetrachloroethene (PCE)
Naphthalene
2-Methylnaphthalene



Push Configuration

Ready-To-Sample Configuration

BENEFITS

- INCREASED NUMBER OF COMPOUNDS
- INCREASE SPEED OF ANALYSIS
- INCREASED VERSATILITY

MILESTONES

- 08/96: COMPLETE LABORATORY TESTING OF ANALYTE BEHAVIOR IN SOILS
- 10/96: COMPLETE DESCRIPTION OF ANALYTE BEHAVIOR IN SOILS

SERDP
Strategic Environmental Research and Development Program
A Partnership to Improve the Environment

Demonstration of SCAPS In-Situ Thermal Volatile Organic Chemical Analysis System for Rapid Characterization of Solvent and POL Contaminated Sites

Lead Organization:
U.S. Army Environmental Center
Aberdeen Proving Grounds, MD 21010-5401

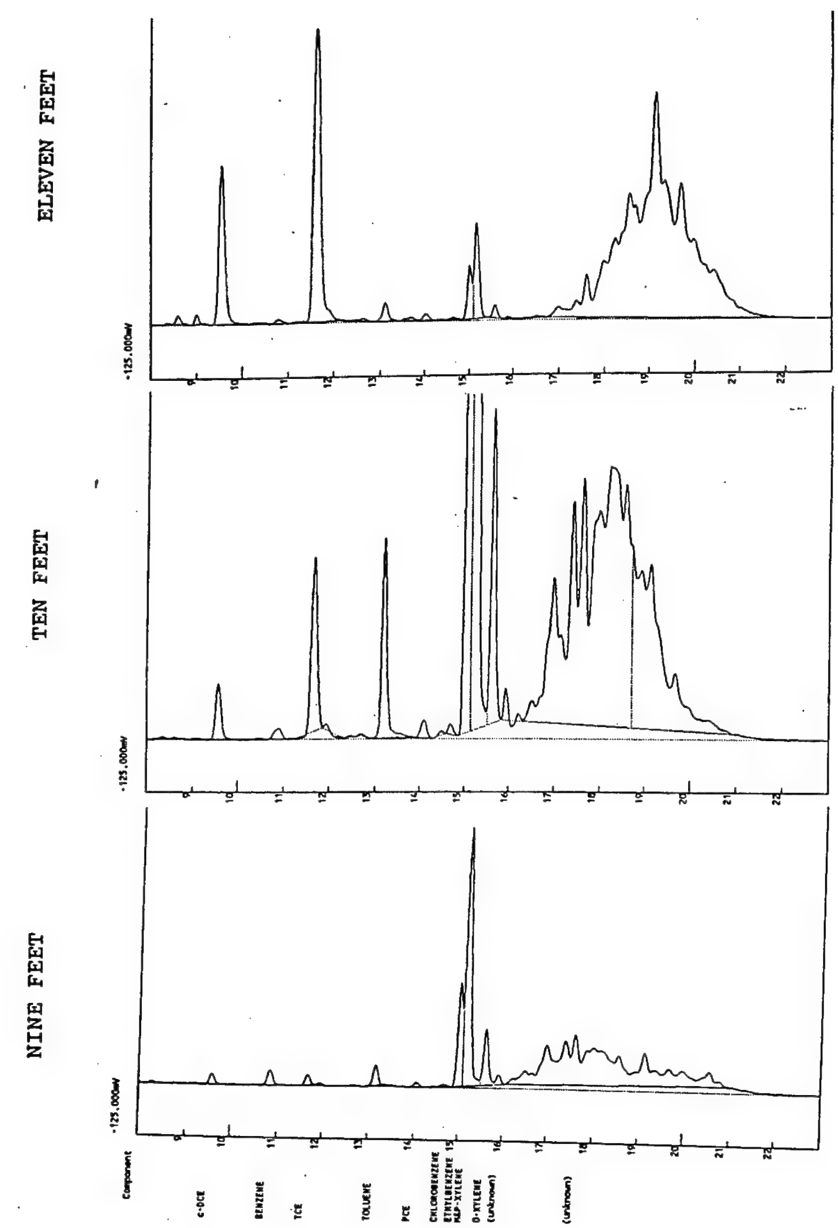
POC: Mr. George E. Robitaille
SFIM-AEC-ETP
Voice: 410-612-6865
FAX: 410-612-6836

TECHNICAL DESCRIPTION

- In-Situ Thermal Desorption of Soil VOC's
- Field Analysis of VOC's
  - Simple VOC Detectors
  - Gas Chromatograph or Ion-Trap
  - Mass Spectrophotometry
- Vadose Zone and Saturated Zone Sampling
- Vapor Sampling in Vadose Zone

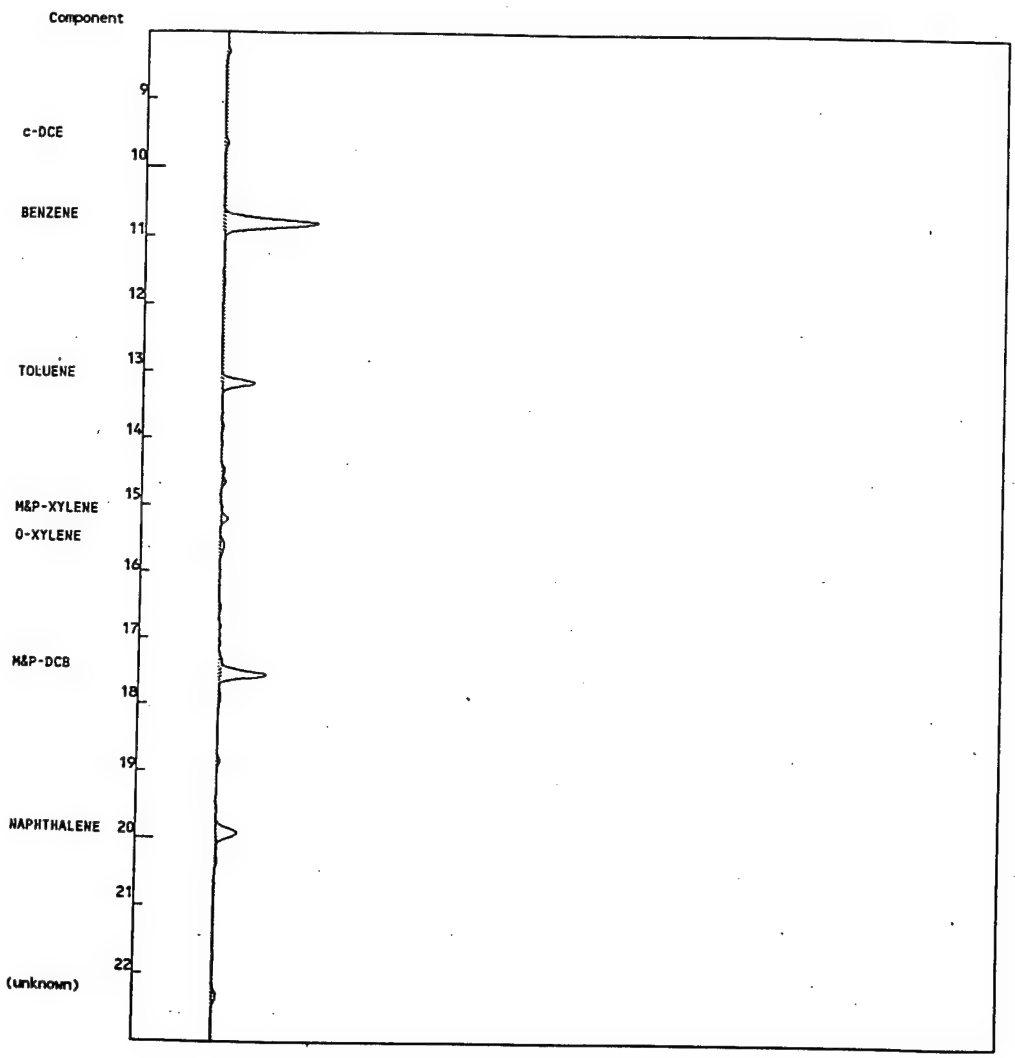
VERIFICATION

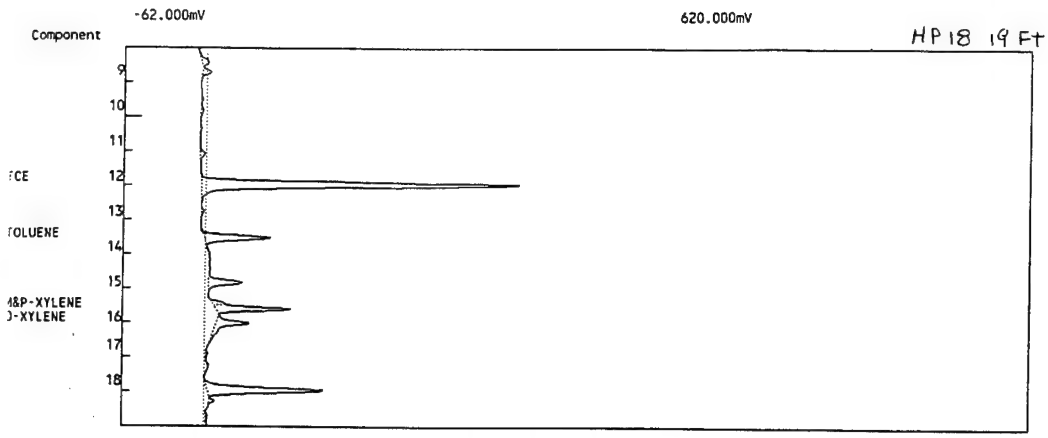
- Laboratory Analysis of Verification Soil Samples
- Compare with VOC Analysis System Results



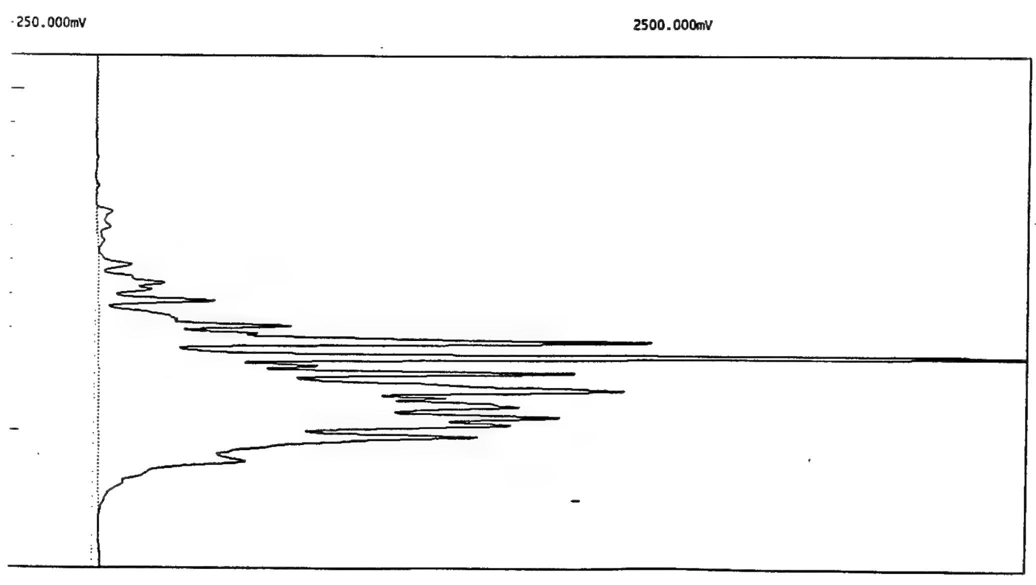
ELEVEN FEET
TEN FEET
NINE FEET
Component
c-DCE
BENZENE
TCE
TOLUENE
PCE
CHLOROBENZENE
ETHYLBENZENE
M&P-XYLENE
O-XYLENE
(unknown)
(unknown)

Lab name : SCAPS fieldtrial DOVER DE
Analysis date : 05/15/1995 07:22:42
Data file : P5135_5.CHR (c:\peak3\data1)
Sample : 17-5vt28 vap-5.75ft tp11
Comments : VAPOR SAMPLE, 30 MINUTES
: HOLE # 17, 5.75 FT
: CONCENTRATION IN NG MASS ON TRAP
:
:





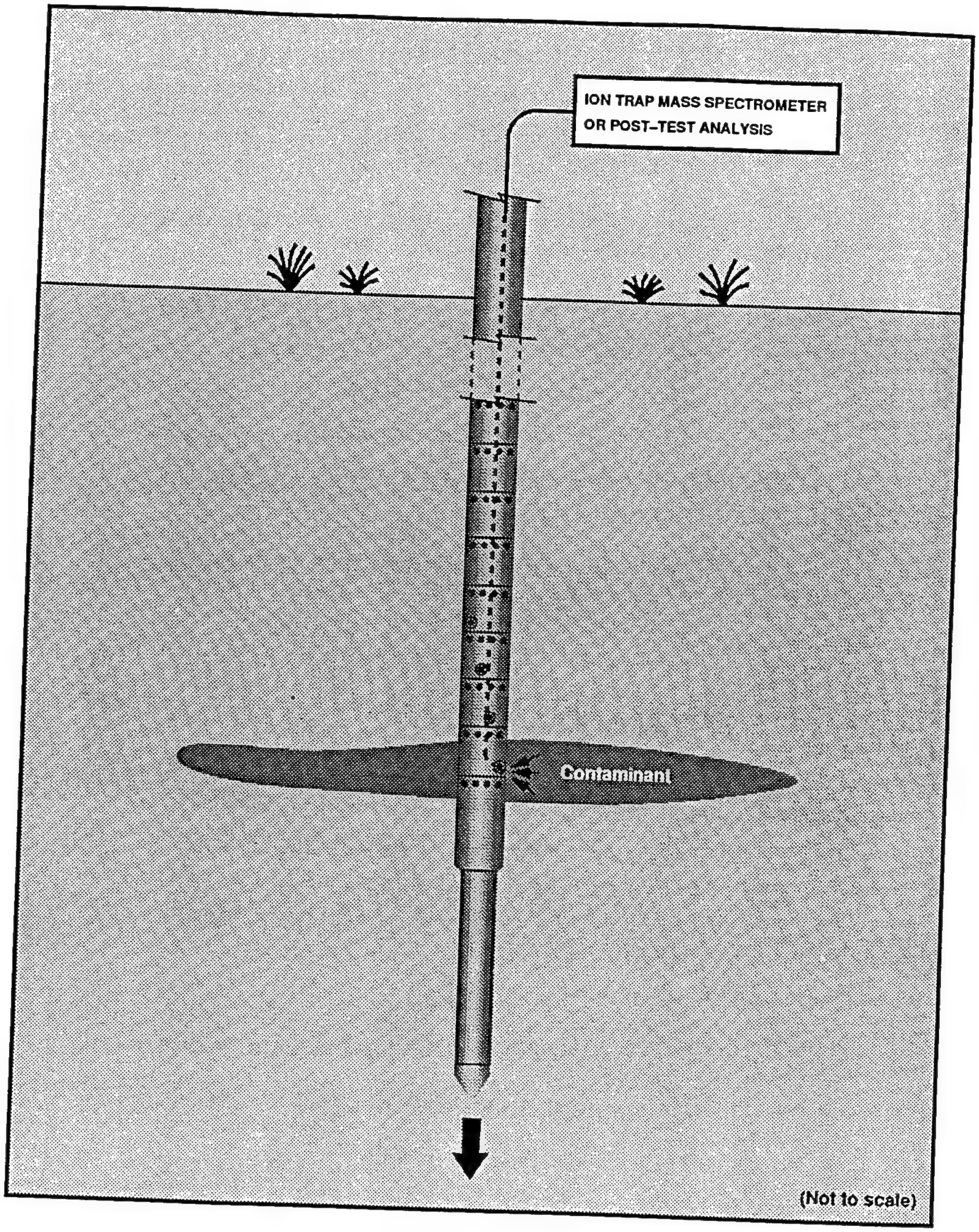
SITE ID	SAMPLE ID	LOCATION	DEPTH FT BGS	c-DCE ng/g	TCE ng/g	TOLUENE ng/g	PCE ng/g	T-XYLENES ng/g	GW DEPTH FT BGS
APG 5234	HP18 S15 T26	HP18	15	ND	590	70	ND	90	17.8
APG 5235	HP18 S16.5 T32	HP18	16.5	ND	581	46	ND	45	17.8
APG 5235	HP18 S19 T39	HP18	19	ND	781	44	ND	77	17.8



THE MULTIPORT SAMPLER

OBJECTIVES

- Improve operational capabilities of Multiport Sampler
- Field Test the Multiport Sampler
- Model behavior of analyte in region of sampling port (In preparation of laboratory investigation)


ION TRAP MASS SPECTROMETER
OR POST-TEST ANALYSIS
Contaminant
(Not to scale)

ACCOMPLISHMENTS

- Paper for ASTM Special Technical Publication 1282 entitled, "The Multiport Sampler: An Innovative Sampling Technology."
- WES Technical Report entitled, "Design, Development, and Operation of the Multiport Sampler."
- Modified the MPS to improve its' operational capabilities:
  - a) Eliminated the twelve screw attachment design (three dowel pins have replaced the screws).
  - b) Fabricated new modules, ports, pistons, and adapters.
  - c) Developed procedure for measuring volume drawn through the Contaminant Trap.
  - d) Modified control panel to allow detection of port leakage.
  - e) Fabricated two cone mandrels.

ACCOMPLISHMENTS (Cont'd)

- Field test at Dover AFB, Delaware.
- Initiated numerical analysis of analyte behavior in region surrounding sampling port.

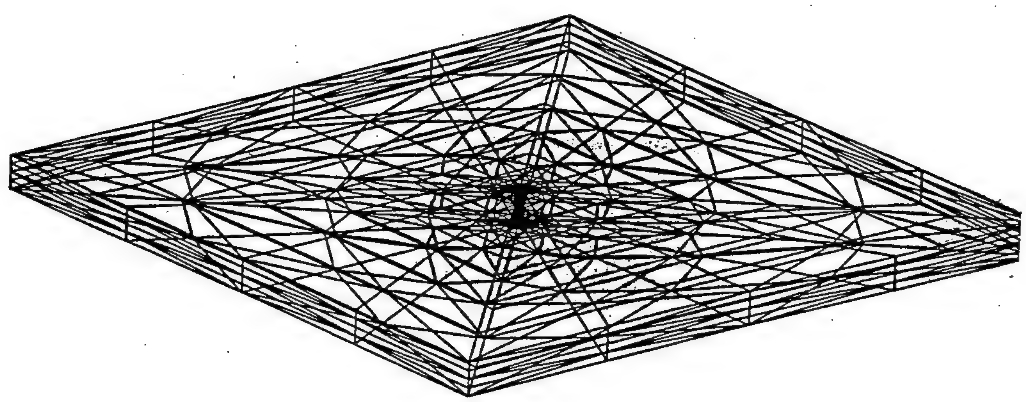
FIELD TEST

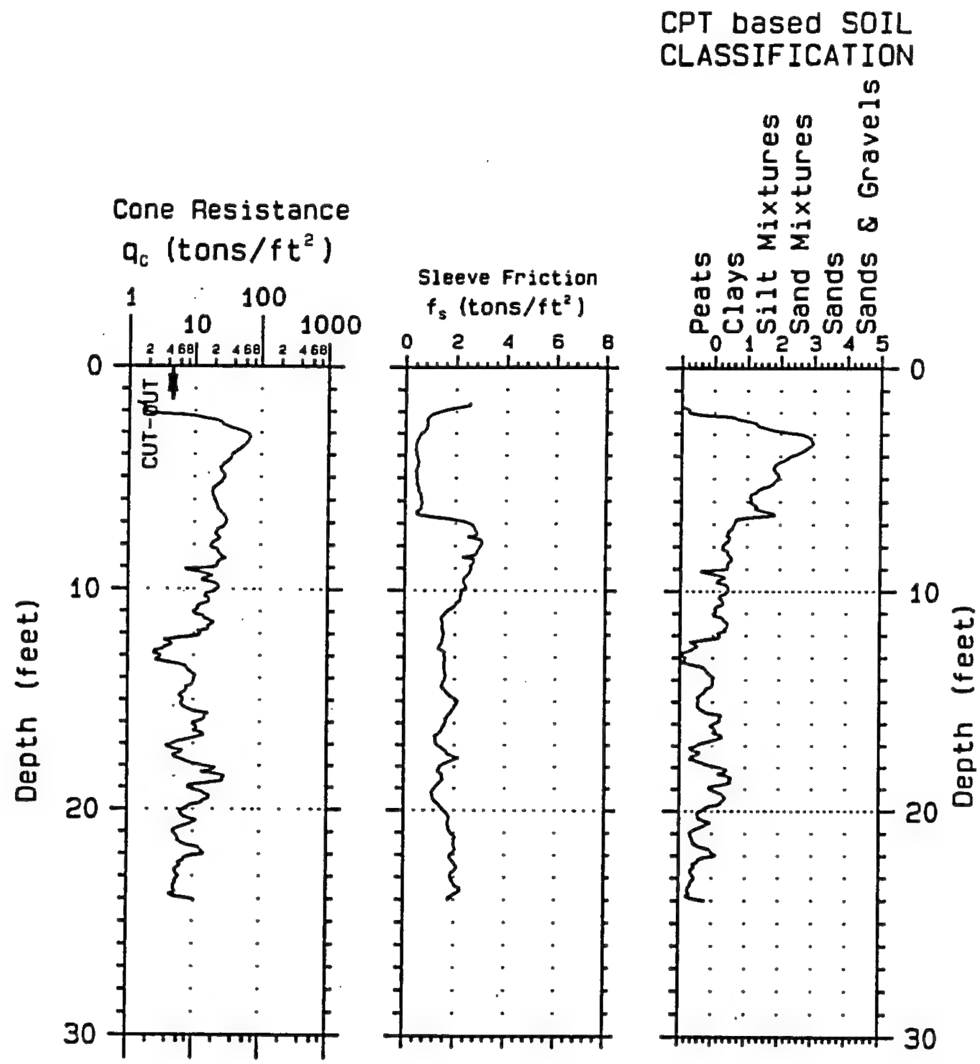
DOVER AFB, DELAWARE

1-5 MAY 95

Multiport Sampler Direct Measurement and Contaminant Trap Field Data Taken at Dover AFB, Delaware

Hole	Data Type	Depth	1.1.1-TCA	TCE	Benzene	Toluene
DVRMPS1	CT	7.83	5990	1351	0	0
DVRMPS1	DM	8.00	12910	206	0	0
DVRMPS1	DM	9.00	11640	109	0	0
DVRMPS3	CT	4.83	423	0	0	35
DVRMPS3	DM	5.00	546	0	14	23
DVRMPS4	CT	5.83	1537	0	274	66
DVRMPS4	DM	6.00	3063	0	6	28
DVRMPS7	DM	7.00	166350	4560	0	0
DVRMPS7	DM	8.00	86770	2382	0	0
DVRMPS8	DT	7.0-9.0	1000-1250	0	N/A	N/A
DVRMPS8	CT(C-18)	21.5	1	0	0	0




CPT based SOIL CLASSIFICATION
Cone Resistance
q_c (tons/ft^2)
1
10
100
1000
2 4 68
CUT-OUT
Sleeve Friction
f_s (tons/ft^2)
0 2 4 6 8
Peats
Clays
Silt Mixtures
Sand Mixtures
Sands
Sands & Gravels
0 1 2 3 4 5
Depth (feet)
0
10
20
30

NUMERICAL MODELING OF ANALYTE IN REGION OF SAMPLING PORT

Modeling Parameters

- Permeability of moist sand to air
- Mass transfer rate of TCE from water to air
- Compressibility of air
- Maximum concentration of TCE in water
- Molecular diffusion of TCE in air
- Dispersivity (relative to flow direction)
- Effective porosity
- Maximum concentration of TCE in air
- Mesh dimensions

RESEARCH AREA VII DATA PROCESSING METHODOLOGIES

Milestones	Schd	Reschd	Comp
• Complete development of data processing methodology	10/94	11/94	11/94
• Complete development of enhanced data acquisition, analysis, and visualization software	03/96		
• Complete testing and user review of enhanced software	06/96		

SCAPS DATA PROCESSING FRAMEWORK

- **Objective**
  - To develop acquisition, analysis, and visualization software to exploit the capabilities of emerging sensor and sampler technology
- **Software Components**
  - Acquisition and real-time display
  - Processing, analysis, and database management
  - 3D visualization

SCAPS DATA PROCESSING FRAMEWORK

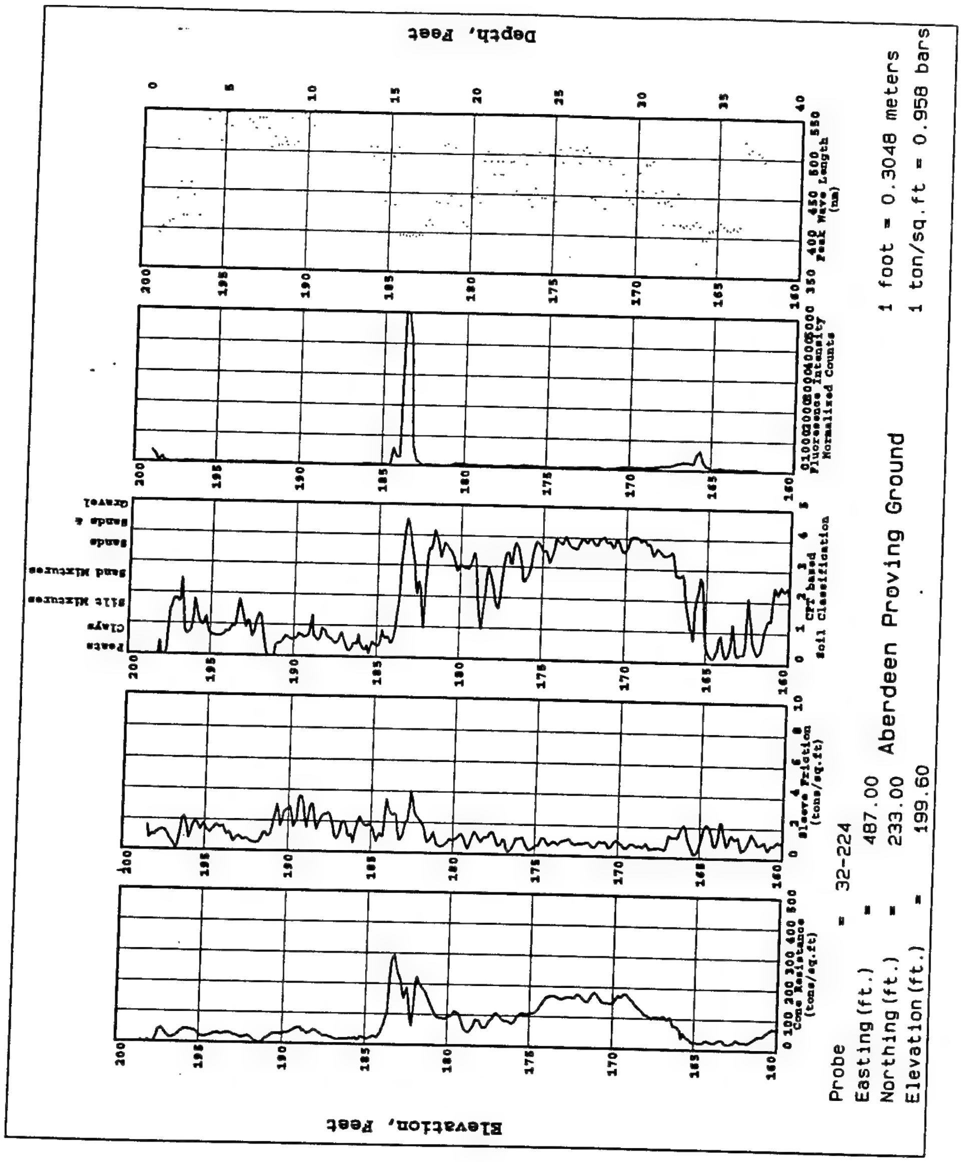
- **Hardware Architecture**
  - Acquisition - MS-DOS PC
  - Processing/Visualization - Unix workstation with 24-bit z-buffered graphics (may be ported to PC in the future)
- **Approach**
  - Develop a flexible software architecture that incorporates a graphical user interface and a well-defined database structure to facilitate incorporation of new sensors

SCAPS DATA PROCESSING FRAMEWORK

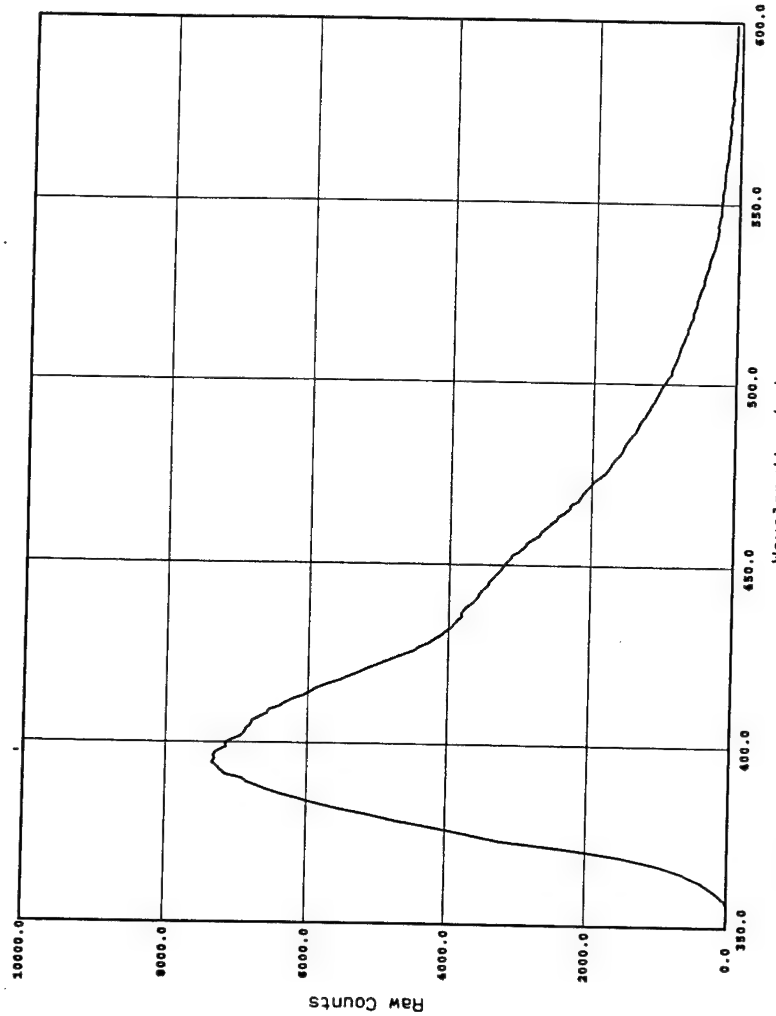
- **Approach** (cont.)
  - Continue development of the SCIRT (MSU) 3D visualization software
  - Maintain links to Earthvision (DGI) software
  - Incorporate new sensors
  - Develop capability for storage/retrieval of SCAPS database on CD-ROM
  - Investigate porting processing/visualization software to PC

ACCOMPLISHMENTS

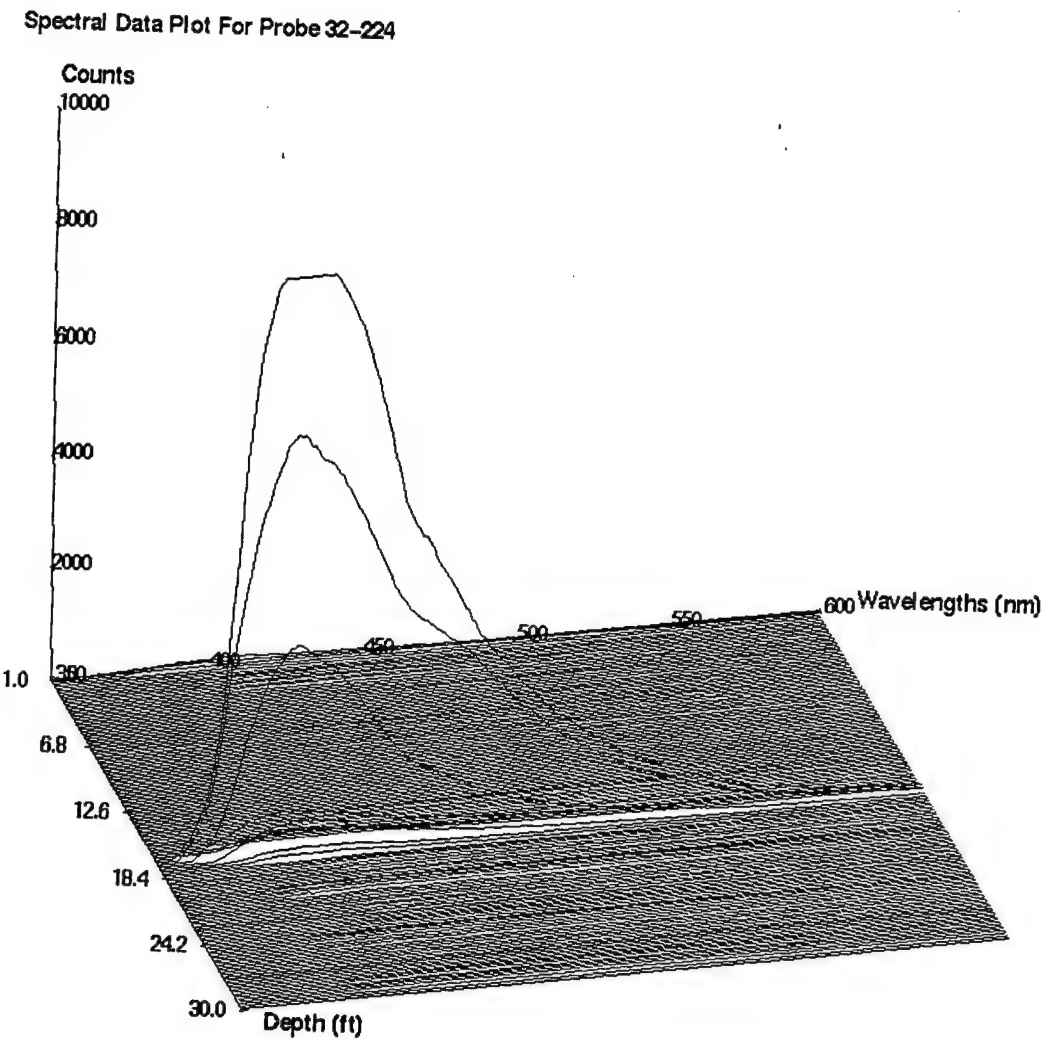
- **Completed initial version of software that incorporates a graphical user interface and database structure and provides an interface to SCIRT and Earthvision**
- **Demonstrated 3D visualization in the field**
- **Modifications to SCIRT**
  - Improve interpolation algorithms
  - Display a site map on 3D plume
  - Conversion to open GL



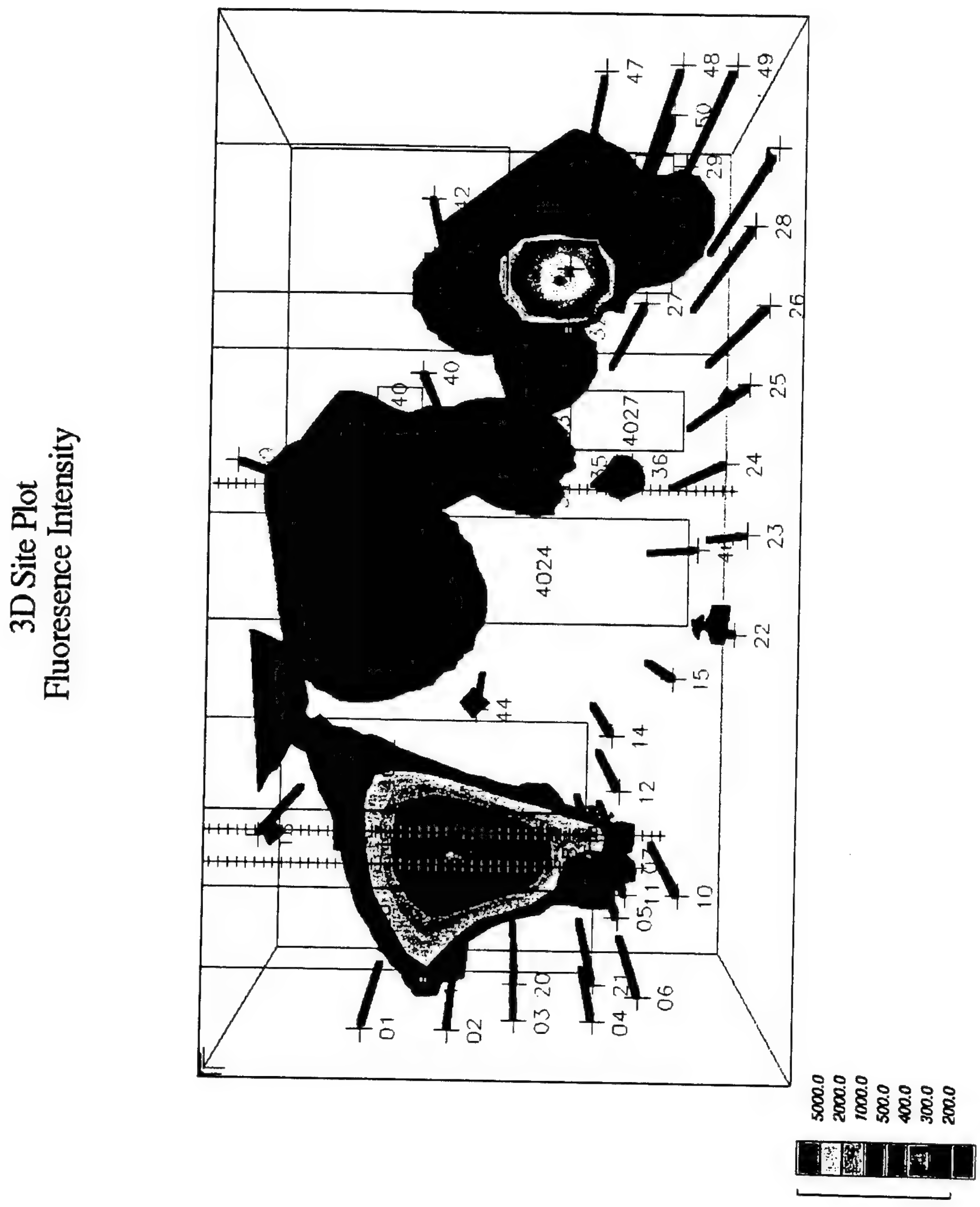
Depth, Feet
Elevation, Feet
Cone Resistance (tons/sq.ft)
Sleeve Friction (tons/sq.ft)
CPT based Soil Classification
Peats
Clays
Silt Mixtures
Sand Mixtures
Sands
Sands & Gravel
Fluorescence Intensity Normalized Counts
Peak Wave Length (nm)
Probe = 32-224
Easting (ft.) = 487.00
Northing (ft.) = 233.00
Elevation (ft.) = 199.60
Aberdeen Proving Ground
1 foot = 0.3048 meters
1 ton/sq.ft = 0.958 bars

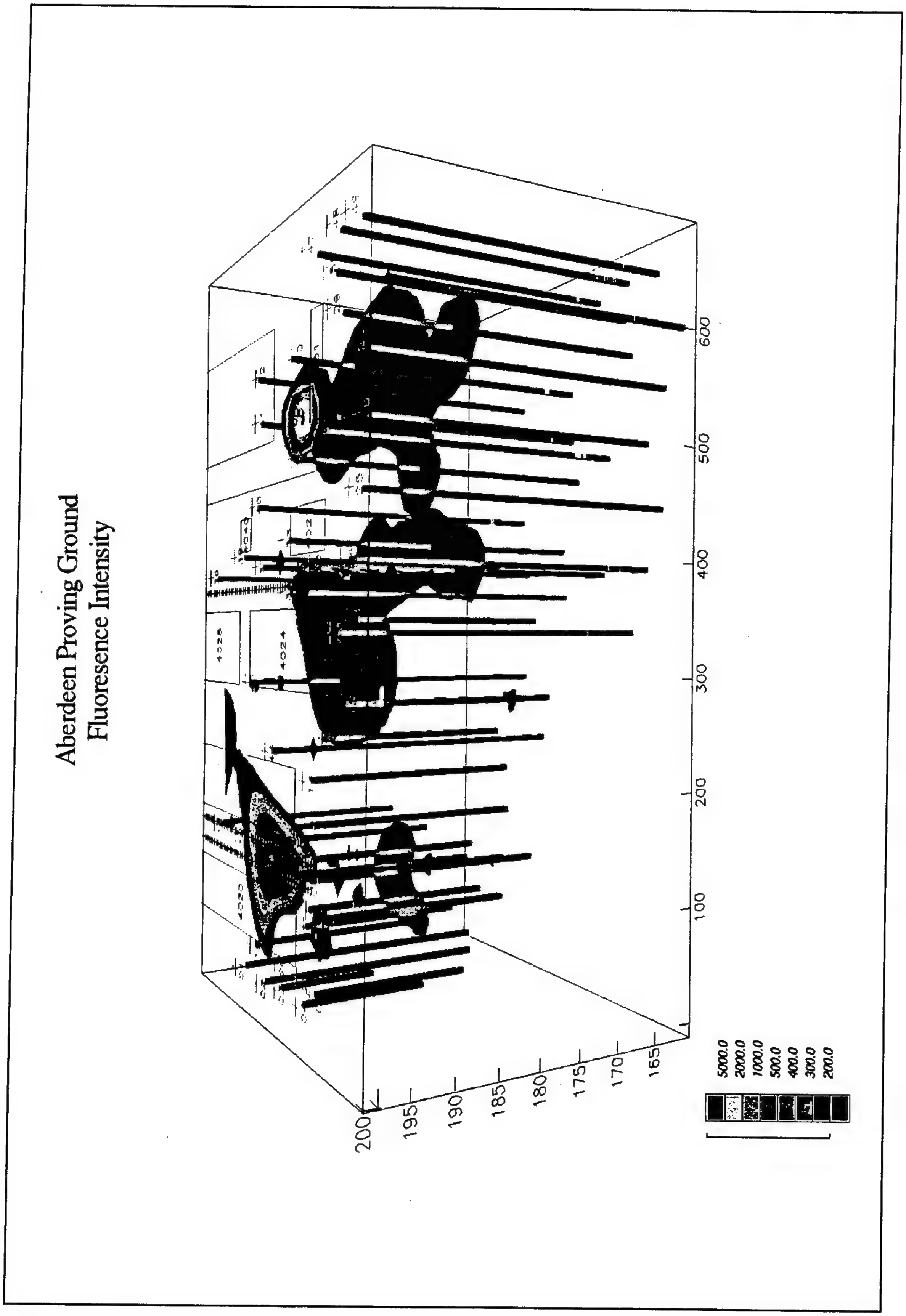


Spectral Data Plot at a depth of 16.0 ft. for Probe 32-224



Spectral Data Plot For Probe 32-224
Counts
10000
8000
6000
4000
2000
1.0
6.8
12.6
18.4
24.2
30.0
Depth (ft)
350
400
450
500
550
600
Wavelengths (nm)


3D Site Plot
Fluoresence Intensity
4024
4027
5000.0
2000.0
1000.0
500.0
400.0
300.0
200.0


Aberdeen Proving Ground
Fluoresence Intensity
100
200
300
400
500
600
165
170
175
180
185
190
195
200
5000.0
2000.0
1000.0
500.0
400.0
300.0
200.0

ACCOMPLISHMENTS

- Completed software to acquire and display data from explosives probe
- Procured and tested a CD-R system
- Investigated issues related to porting processing/visualization software to a PC

FUTURE WORK

- Complete SCIRT modifications and test
- Incorporate new sensors
- Make improvements to acquisition, processing, and database management software
- Evaluate the use of the groundwater modeling system (GMS) for SCAPS
- Documentation
- Port software to Windows NT-based PC

Technology Demonstration Implementation

- OBJECTIVE: To demonstrate SCAPS sensors, sampling hardware, and associated data processing technologies
- APPROACH: Conduct demonstrations with SCAPS, comparing SCAPS data with data obtained through traditional sampling and analysis methods

DoD/National Environmental Technology Demonstration Program

SITE LOCATIONS

Use of DoD NETDP Test Sites

- Groundwater Remediation Field Laboratory National Test Site (Dover AFB, DE) - LIF, VOC Probes
- Natural Attenuation Test Site (Columbia AFB, MS) - LIF
- Port Hueneme, CA - LIF
- Wurtsmith AFB, MI - LIF
- Volunteer Army Ammunition Plant - Explosives Sensors
- McClellan AFB, CA - LIF
- Others TDB

Field Testing & Demonstrations

	Comp.
• EPA SITE Demonstration of LIF POL Sensor	09/94
• Initial Field Testing of Explosives Sensor (LAAP)	10/94
• Field Testing of Explosives Sensor (Pantex)	03/95
• Field Testing / Demonstration of Explosives Sensor (VAAP)	04/95

Field Testing & Demonstrations

	Schd.
• Conduct Columbus AFB Demonstration of POL Sensor	05/95
• Conduct Dover AFB Demonstration	05/95
• Complete Initial Field Evaluation of Thermal Desorption VOC Sampler	05/95
• Conduct Port Hueneme, CA Demonstration	06/95
• Conduct Wurtsmith AFB, MI Demonstration	07/95
• Conduct Field Test of Explosives Sensor (Camp Navajo, AZ)	08/95
• Complete Field Demonstration of Improved Multiport Sampler	10/95

(Continued)

Field Testing & Demonstrations

	Schd.
• Conduct Demonstration of SCAPS Electrochemical Probes with Associated Software	01/96
• Conduct Validated and Demonstrated Enhanced SCAPS LIF POL Sensor and Software	03/96
• Initiate Field Testing / Demonstrations of FORS System	04/96
• Complete Demonstrations of Improved Sampler Technologies	10/96
• Conduct Demonstrations of LIBS Sensor System	12/96
• Complete Demonstrations of FORS System	01/97
• Conduct Demonstration of PF / LIF Explosives Sensor System	06/97

TRANSITION PLAN

- R&D results will be documented in peer-reviewed journals, technical conference proceedings, and agency technical reports
- Yearly meetings of peer review panel, researchers, developers, and users will be conducted, and proceedings published
- Field demonstrations will be conducted and results will be documented in technical reports
- Validated sensors and supporting SCAPS technologies will be made available to Government SCAPS users, complete with documentation, O&M manuals, and onsite training
- Tri-Services will continue to aggressively pursue commercialization of SCAPS technology through licensing agreement, CRADA's, and TRP

EXPECTED PAYOFF

- Provide rapid, cost effective methods to characterize sites
- Significantly increase the number and types of contaminated sites that can be characterized by SCAPS
- Maximize cost savings by accelerating the fielding of new SCAPS technologies to support remediation efforts
- Increase acceptance of SCAPS as a rapid field screening tool by users, regulators, and public

Technology Demonstration/Implementation

Objective: Demonstrate SCAPS Sensors, Specifically Tunable LIF (ROST), Sampling Hardware, and Associated Data Processing Technologies With Respect to Jet Fuels and Gasolines Having Lighter Aromatic Compounds (BTEX).

Approach: Conduct SCAPS Demonstrations With Tunable LIF System, Comparing Data to that Obtained Through Traditional Sampling and Analyses Methods.

Payoff: Validation of SCAPS Performance and Cost Effectiveness for Site Characterization From a Users Perspective (KC CoE) and to Facilitate User and Regulatory Acceptance.

Technology Demonstration/Implementation Status

Making Use Of Kansas City CoE SCAPS

- **Transitioned Laser - Sep 94**
- **Subcontract to DTI for Tunable Laser Support - May 95**
- **Hardware Upgrade - May 95**
- **Integrate Tunable Laser - June 95**
- **Provide Training, Including on the Job - May/June 95**

Wurtsmith AFB National Test Site Demonstration Completed

- **Firefighter Training Area Site Having Mixture of Contaminants**
- **Innovative Hollow Stem Auger/Split Barrel Sampler**
  - **Ensures What is Sensed is Sampled!**
- **Sample Analyses and Chemical Data Analysis Ongoing**

Dover AFB National Test Site Demonstration Initiated

- **Hydrant Fuel System Contamination Believed to be Just JP-4**
- **Site Also Has Sands/Gravels With Shallow Groundwater**

Technology Demonstration/Implementation Status (cont.)

Columbus AFB, MS
- SERDP Funded Natural Attenuation Test Site (NATS)
- Primarily Sands/Gravels and No Contamination Until Release
- Demonstration Cancelled Due to Delayed Site Approvals

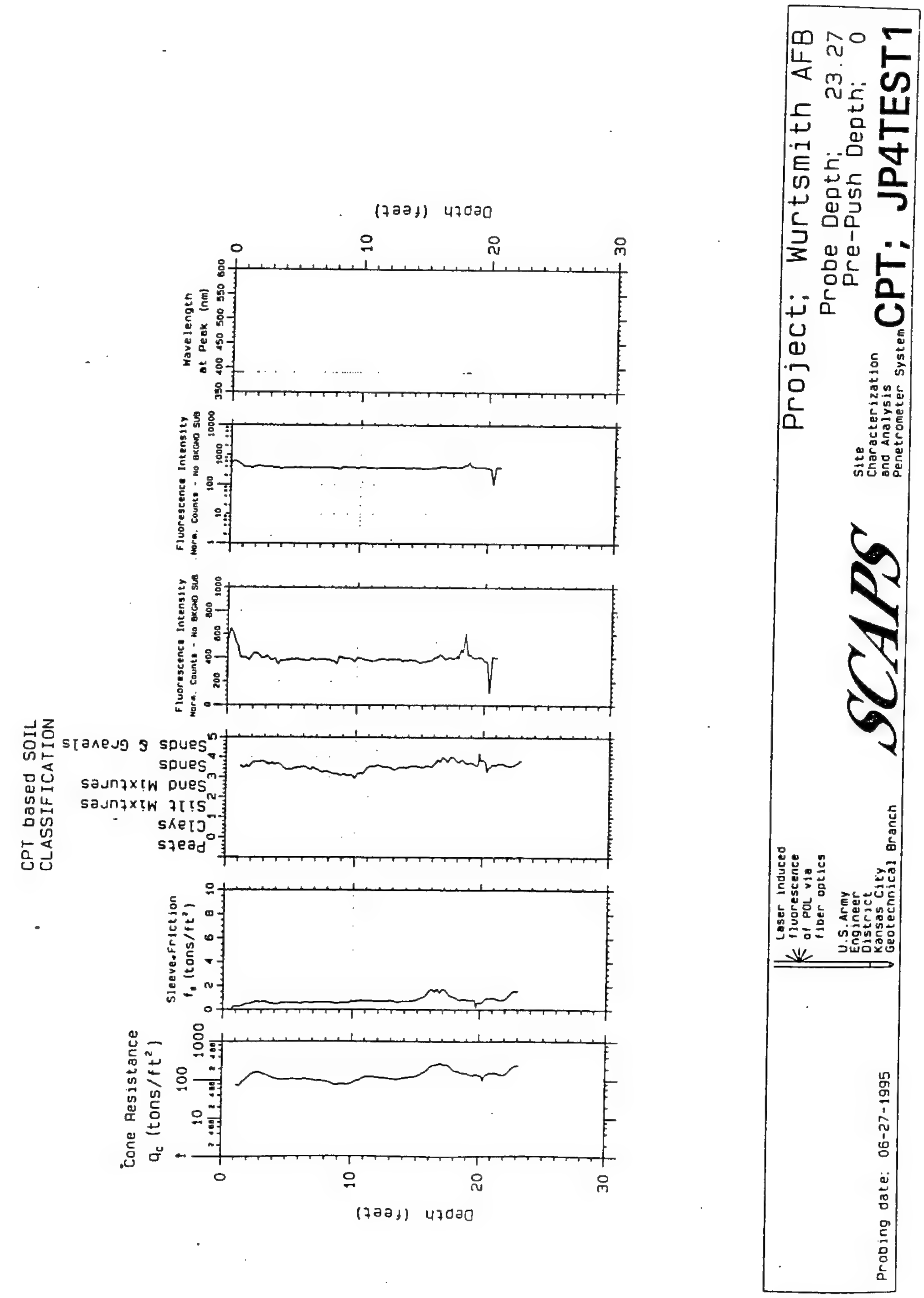
Port Hueneme, CA
- Also Primarily Sands
- Not Selected Due to Excellent Navy Sponsored Demonstration
  - Made Use of ROST System on Navy SCAPS

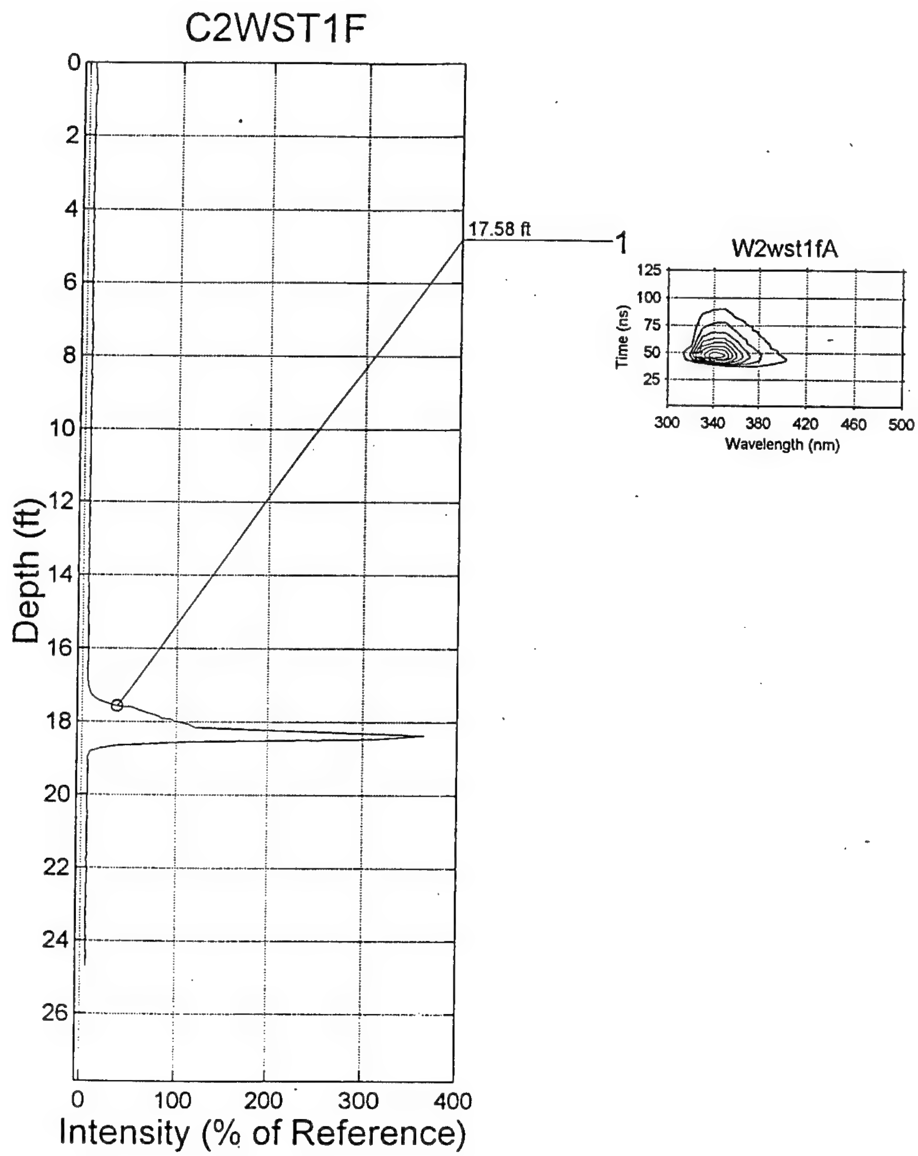
Site Needs
- Emphasize Demos at Sites Having Only Jet Fuel or Gasoline
  - Laser Wavelength at 290nm or Lower
- Heterogenety in Vadose Zone, Especially Fine Grained Soils
  - Sampling Below Water Table Is Problematic

Technology Demonstration/Implementation Status (cont.)

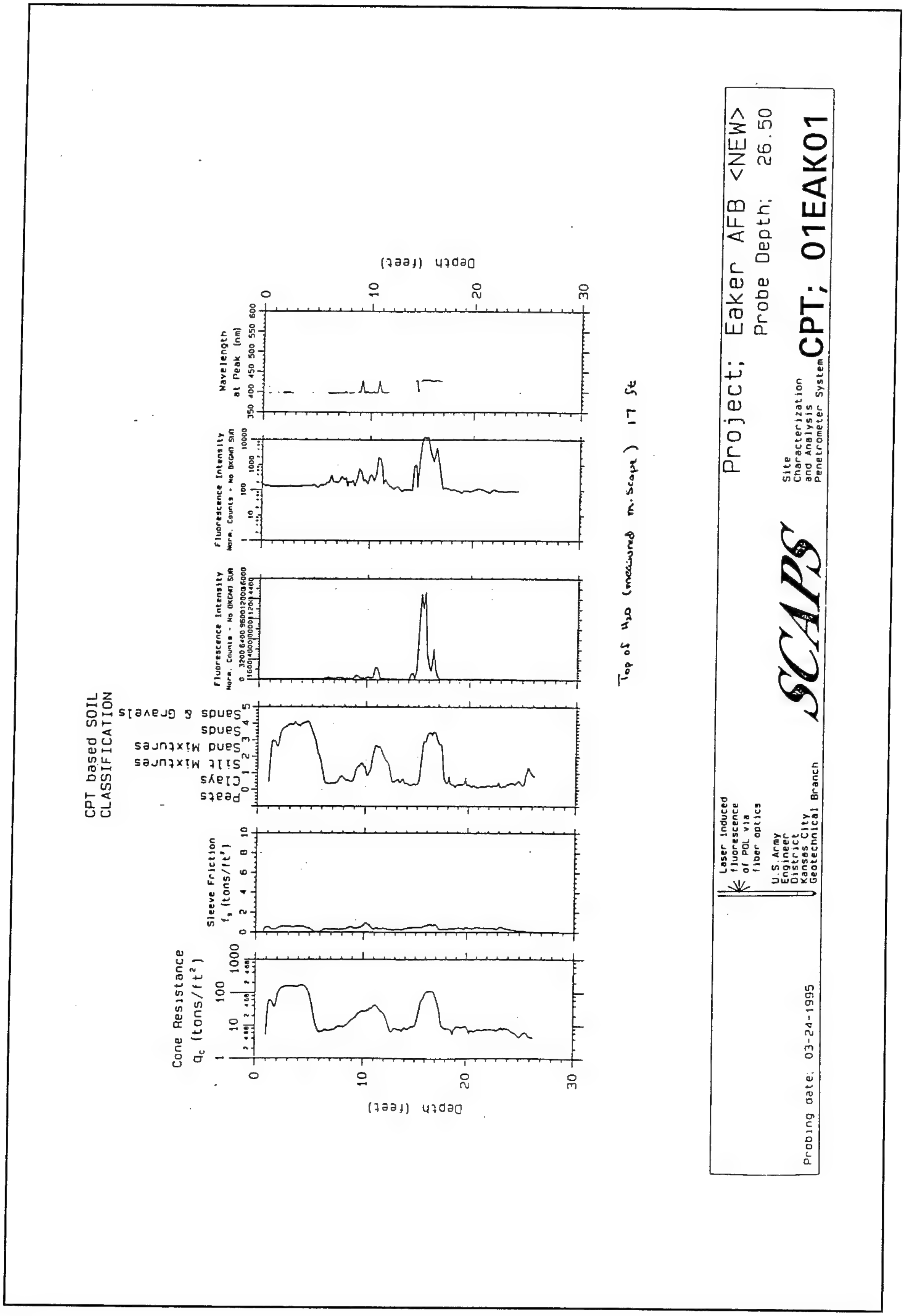
Propose Eaker AFB, AR as Demonstration Site
- Excellent Data Set From AFCEE SCAPS Project
  - Used N_2 Laser
- Gasoline Contamination (Dover Provide JP-4 Site)
- Heterogeneous Soils
  - From Fine Grained (Silt/Clays) to Sands
- Contamination in Vadose Zone Above Water Table

Project Schedule
- National Test Sites
  - Wurtsmith AFB, MI - Jun/Jul 95
  - Dover AFB, DE - Jul/Aug 95
- Eaker AFB, AR - Sep 95
- Complete Laboratory Analyses & Reporting - Sep 95
- Complete Draft Report Delivered - Oct 95
- Project Outbrief To Armstrong Lab & Tri-Services - Nov 95
- Final Technical Report and Project Completion - 31 Dec 95


Project: Wurtsmith AFB
Probe Depth: 23.27
Pre-Push Depth: 0
CPT: JP4TEST1
SCAPS
Site Characterization and Analysis Penetrometer System
Laser induced fluorescence of POL via fiber optics
U.S. Army Engineer District Kansas City Geotechnical Branch
Probing date: 06-27-1995
Cone Resistance q_c (tons/ft^2)
Sleeve Friction f_s (tons/ft^2)
CPT based SOIL CLASSIFICATION
Peats
Clays
Silt Mixtures
Sand Mixtures
Sands
Sands & Gravels
Fluorescence Intensity
Wavelength at Peak (nm)
Depth (feet)



C2WST1F
Depth (ft)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
0
100
200
300
400
Intensity (% of Reference)
17.58 ft
1
W2wst1fA
125
100
75
50
25
Time (ns)
300
340
380
420
460
500
Wavelength (nm)


Project; Eaker AFB <NEW>
Probe Depth; 26.50
CPT; 01EAK01
SCAPS
Site Characterization and Analysis Penetrometer System
Laser induced fluorescence of POL via fiber optics
U.S. Army Engineer District Kansas City Geotechnical Branch
Probing date: 03-24-1995
Cone Resistance q_c (tons/ft²)
Sleeve Friction f_s (tons/ft²)
CPT based SOIL CLASSIFICATION
Peats
Clays
Silt Mixtures
Sand Mixtures
Sands
Sands & Gravels
Fluorescence Intensity
Wavelength at Peak (nm)
Depth (feet)
Top of H_2O (measured m. scope) 17 ft

IMPLEMENTATION:
NAVY SCAPS-LIF PROGRAM

- JUNE 1993 - HQ/NAVFAC INITIATED PROGRAM
- PROGRAM ELEMENTS (TRI-SERVICE COORDINATED)
  - EXPEDITED DUAL-USE OF R&D SYSTEM (EDM-1)
    - SITE WORK (NAVY)
    - REGULATORY ACCEPTANCE (TRI-SERVICES)
  - EXPEDITED TECH TRANSFER
    - LIMITED NAVY ACQUISITION (2 EDMs)
    - COMMERCIALIZATION (CRADA, *ET AL*)
  - PRE-PLANNED PRODUCT IMPROVEMENTS
    - UPGRADED SYSTEMS/PROCESSES
    - NEW SENSORS

ITRC TSRG SCAPS-LIF Brief 3

NAVY PROGRAM ELEMENTS:

EXPEDITED DUAL-USE OF RESEARCH SYSTEM

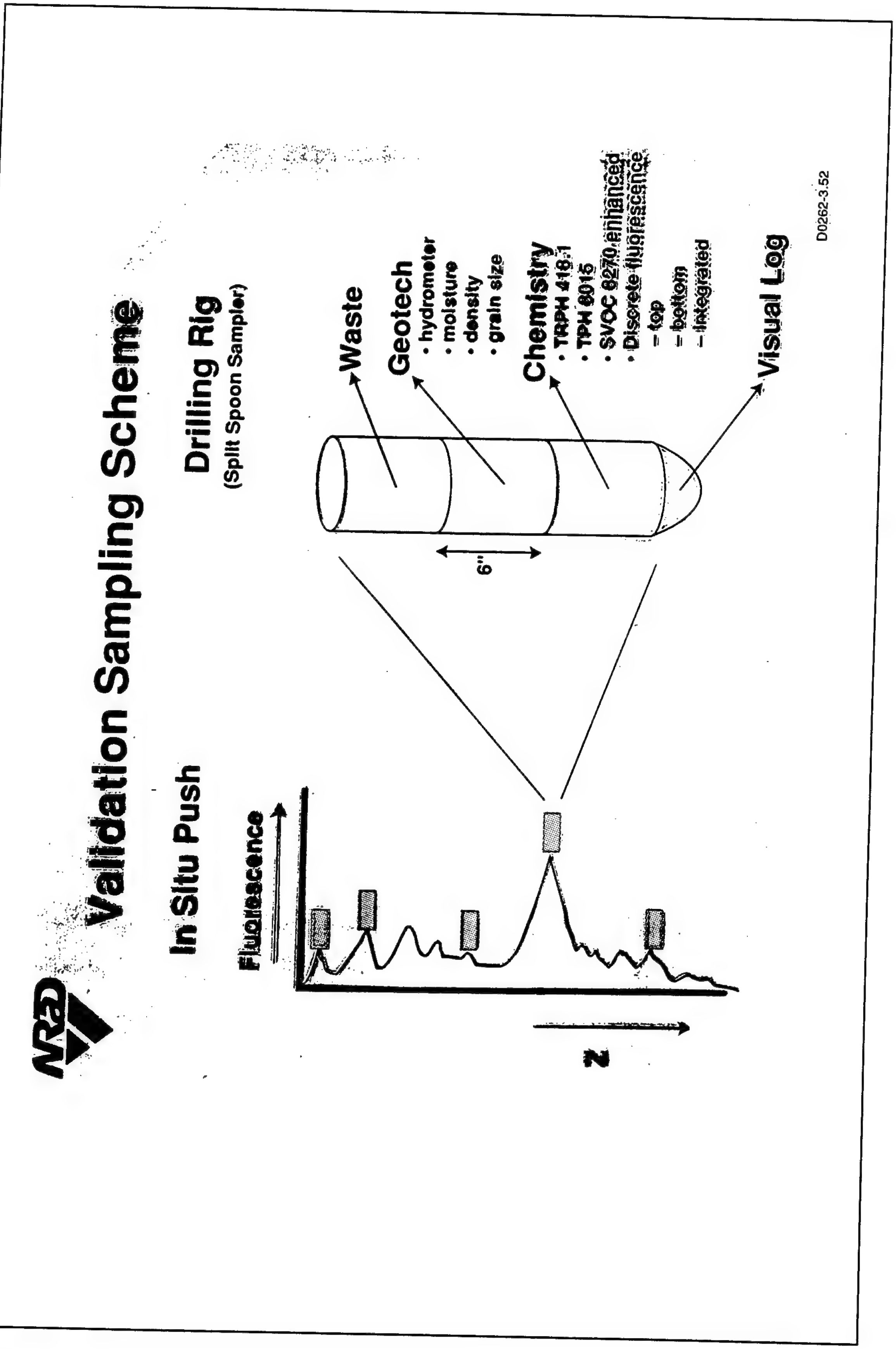
- NAVY SITE WORK
  - HIGH PRIORITY IR SITES WITH DISTINCT SCAPS-LIF VARIABLES
  - 14 SITES
    - *PRODUCTS*: KNOWN/UNKNOWN POLs-FRESH/AGED, SEPERATE/MIXED, ABOVE/BELOW WATER
    - *SOILS*: CLAYS-SANDS-COBBLES, LAYERED MATRICES, DRY-VADOSE-SATURATED ZONES
    - *SITES*: COASTAL/DESERT, URBAN/REMOTE, SHALLOW/DEEP WATER
    - *REGULATORS*: LOCAL, STATE, REGIONAL, FEDERAL
    - *EXAMPLES*: 100 YR OLD REFINERY, ACTIVE/INACTIVE FUEL FARMS, ABANDONED OIL FIELD, FIRE FIGHTER TRAINING SITES, GAS STATIONS, USTs

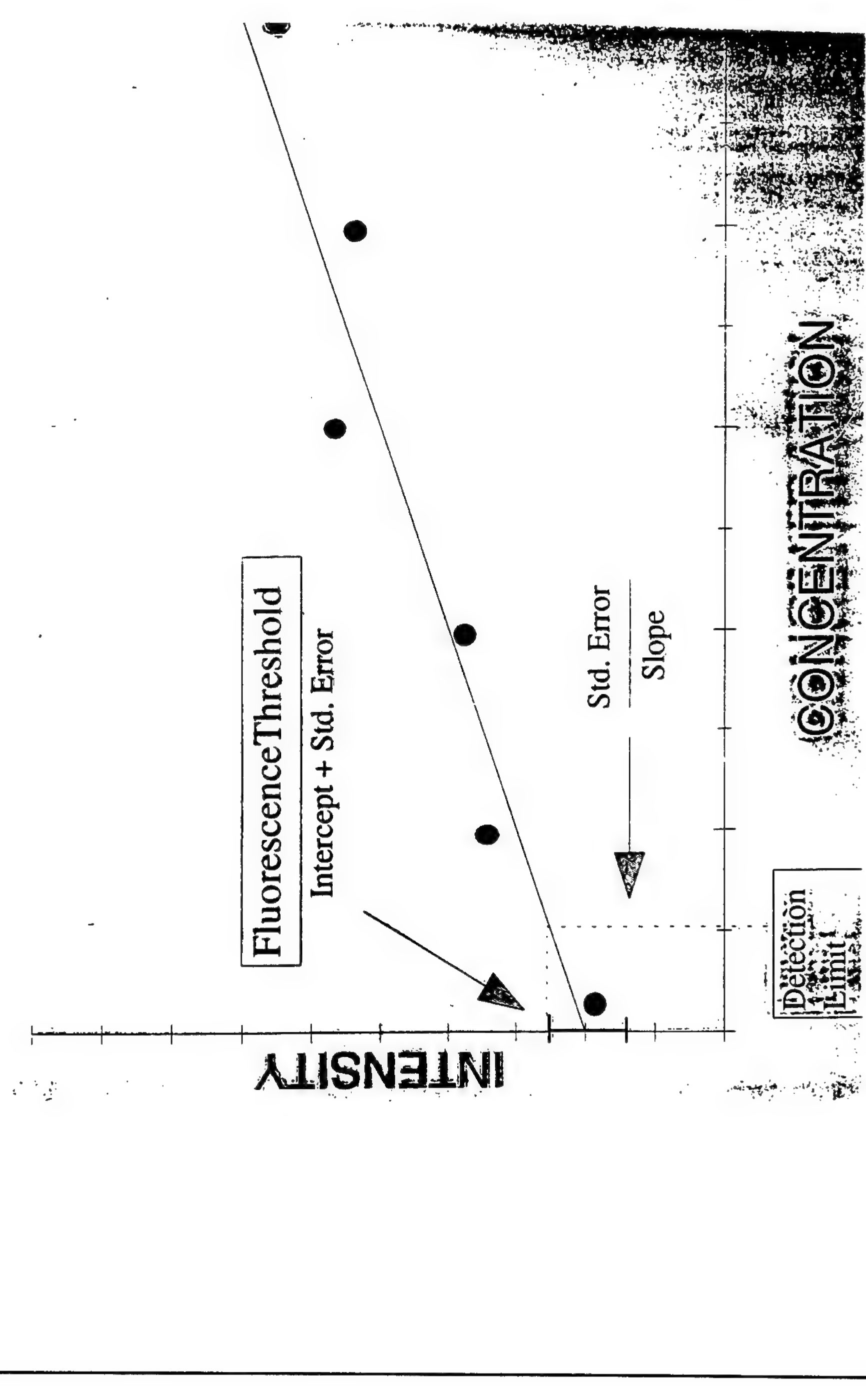
NAVY PROGRAM ELEMENTS:

EXPEDITED DUAL-USE OF RESEARCH SYSTEM

(CONTINUED)

- TRI-SERVICE REGULATORY ACCEPTANCE
  - ESTABLISH HIGH QUALITY VALIDATION DATABASE CONCURRENT WITH FIELD OPS
    - USE/COMPARE TRADITIONAL VS SCAPS-LIF
    - WORK CLOSELY WITH REGULATORS
  - LIF DEMO: THREE INTERLINKED PROGRAMS
    - CAL EPA "CERT" PROGRAM (STATE)
    - WGA/DOIT DEMONSTRATION (REGIONAL)
    - US EPA CONSORTIUM DEMONSTRATION (NATIONAL)
  - EAST COAST REGULATORY ACCEPTANCE
    - REPLICATE/EXTEND VALIDATION PHASE (ESTCP)
    - WORK WITH RPMs AND LOCAL/STATE/REGIONAL REGULATORS
    - INTEGRATE WITH WESTERN RESULTS

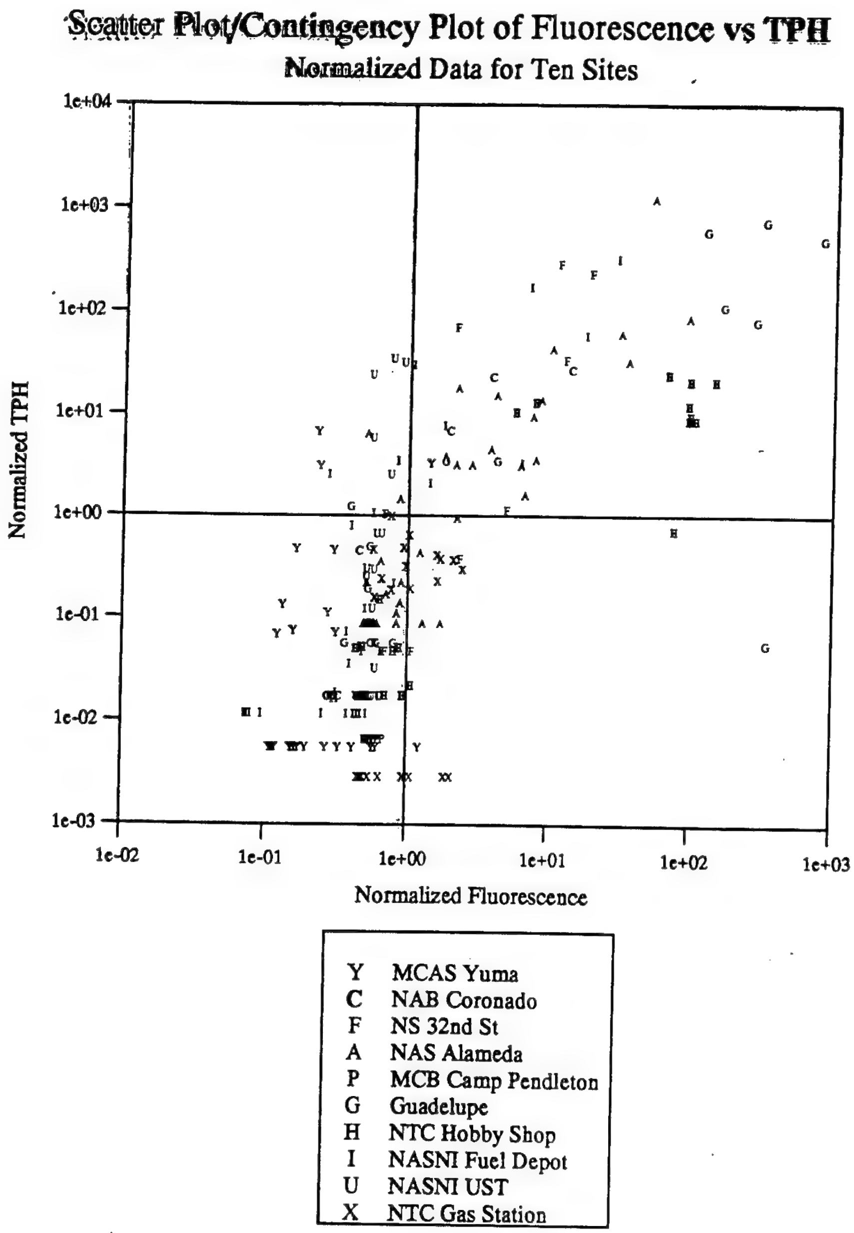

Validation Sampling Scheme
In Situ Push
Drilling Rig
(Split Spoon Sampler)
Fluorescence
Z
6"
Waste
Geotech
· hydrometer
· moisture
· density
· grain size
Chemistry
· TRPH 418.1
· TPH 8015
· SVOC 8270 enhanced
· Discrete fluorescence
– top
– bottom
– integrated
Visual Log
D0262-3.52

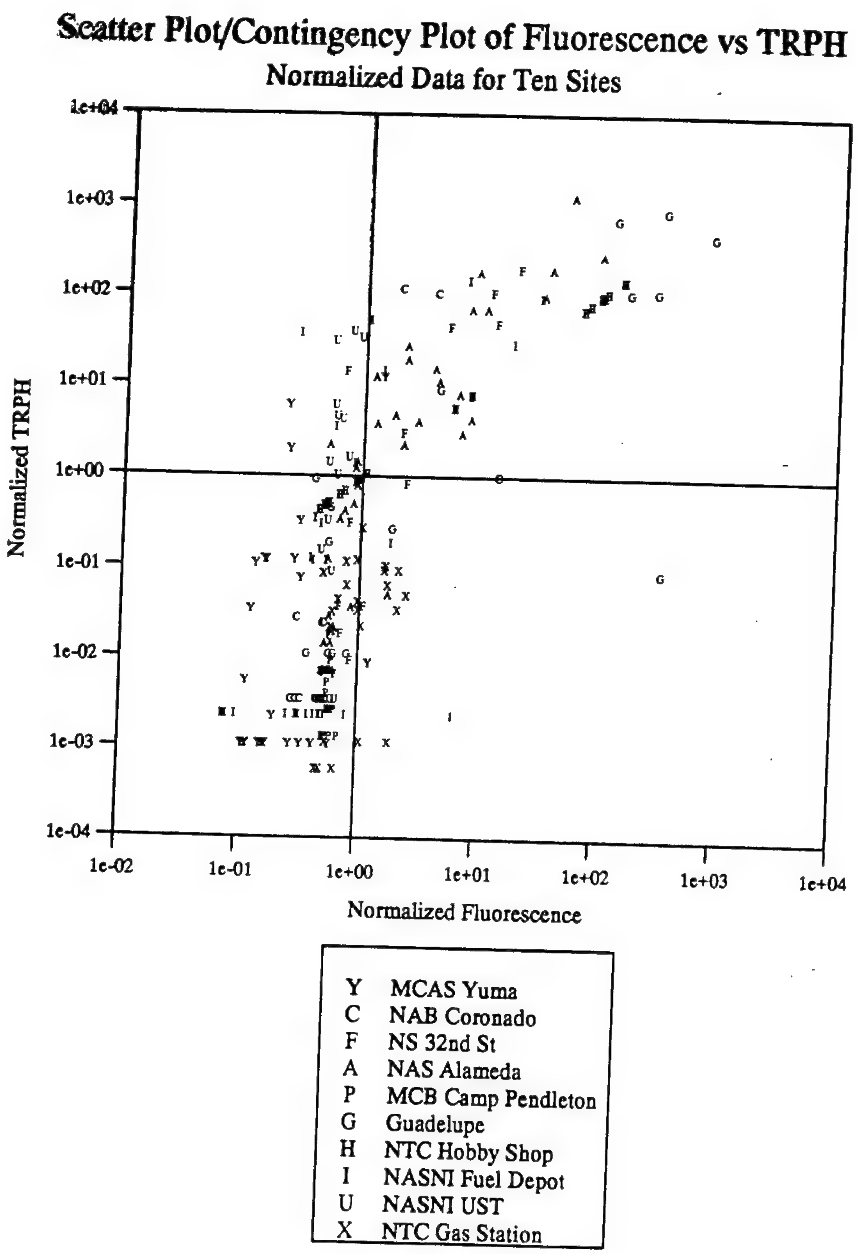

FluorescenceThreshold
Intercept + Std. Error
Std. Error
Slope
Detection Limit
INTENSITY
CONCENTRATION

NRaD

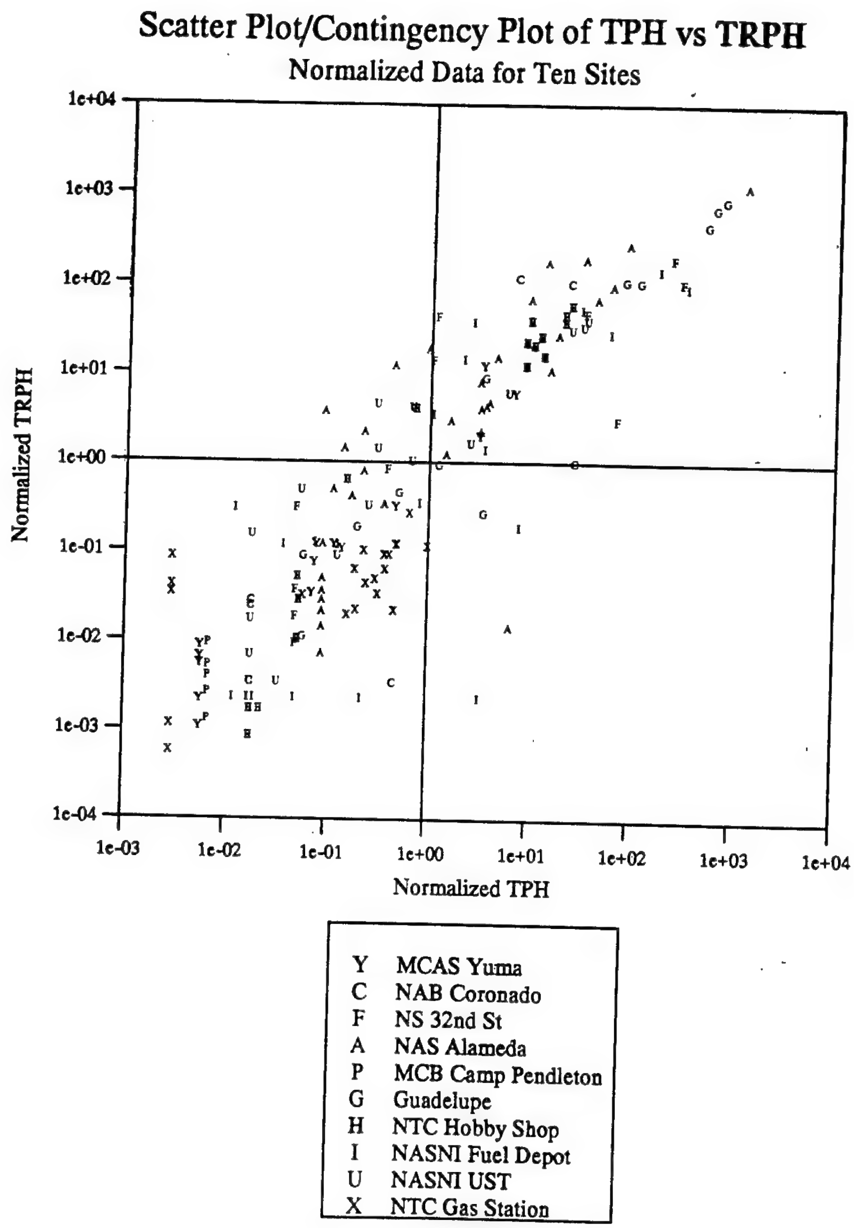
NAVY Validation Sites

- NAS North Island, Fuel Farm
- NS San Diego, FFTF
- NAB Coronado, abandoned fuel farm
- MCAS Yuma
- NAS Alameda, old refinery site
- Camp Pendelton, UST
- NAS North Island, expedited tank yank
- Guadalupe Oil Field
- NTC San Diego, gas station
- NTC San Diego, auto hobby shop


Scatter Plot/Contingency Plot of Fluorescence vs TPH
Normalized Data for Ten Sites
Normalized TPH
1e+04
1e+03
1e+02
1e+01
1e+00
1e-01
1e-02
1e-03
1e-02
1e-01
1e+00
1e+01
1e+02
1e+03
Normalized Fluorescence
Y MCAS Yuma
C NAB Coronado
F NS 32nd St
A NAS Alameda
P MCB Camp Pendleton
G Guadelupe
H NTC Hobby Shop
I NASNI Fuel Depot
U NASNI UST
X NTC Gas Station



Scatter Plot/Contingency Plot of Fluorescence vs TRPH
Normalized Data for Ten Sites
Normalized TRPH
Normalized Fluorescence
1e+04
1e+03
1e+02
1e+01
1e+00
1e-01
1e-02
1e-03
1e-04
1e-02
1e-01
1e+00
1e+01
1e+02
1e+03
1e+04
Y MCAS Yuma
C NAB Coronado
F NS 32nd St
A NAS Alameda
P MCB Camp Pendleton
G Guadelupe
H NTC Hobby Shop
I NASNI Fuel Depot
U NASNI UST
X NTC Gas Station

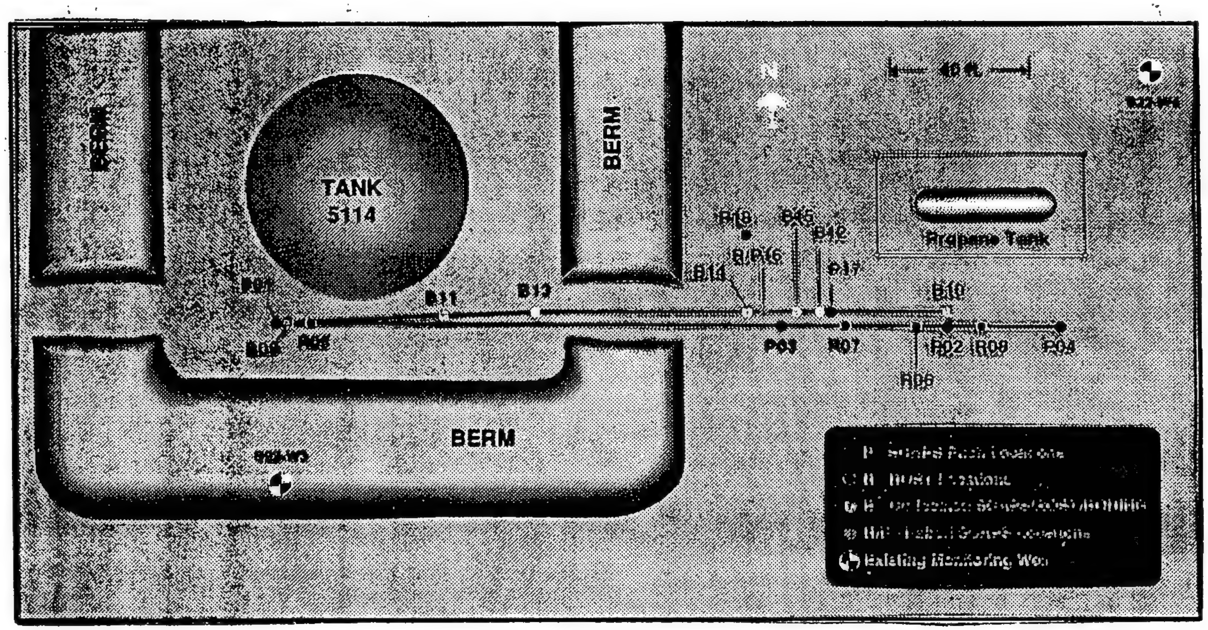


Scatter Plot/Contingency Plot of TPH vs TRPH
Normalized Data for Ten Sites
Normalized TRPH
Normalized TPH
1e-04
1e-03
1e-02
1e-01
1e+00
1e+01
1e+02
1e+03
1e+04
Y MCAS Yuma
C NAB Coronado
F NS 32nd St
A NAS Alameda
P MCB Camp Pendleton
G Guadelupe
H NTC Hobby Shop
I NASNI Fuel Depot
U NASNI UST
X NTC Gas Station

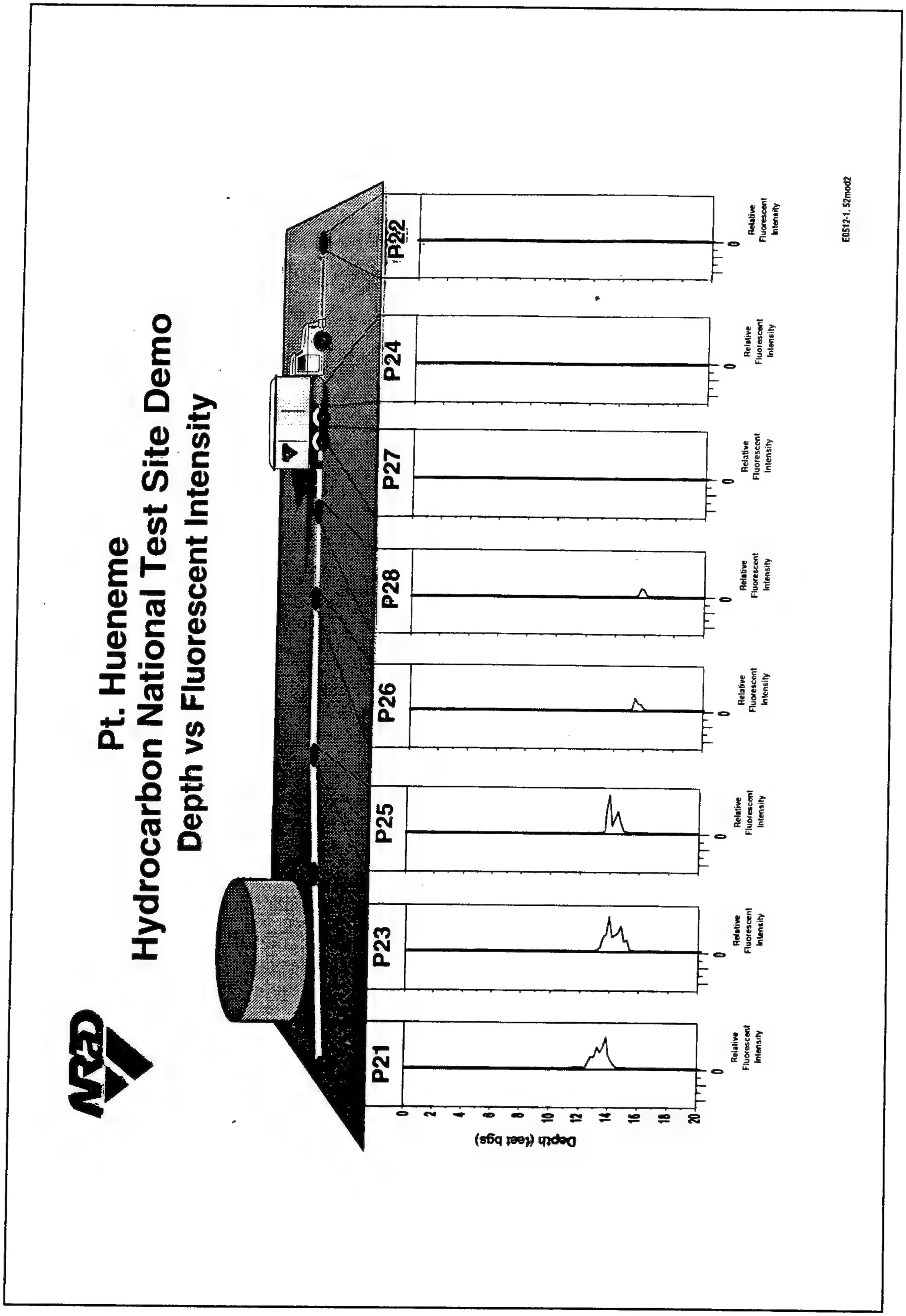
Cumulative Contingency Analysis Summary for 10 Sites (n=219)

Method	% Correct	% False Pos	% False Neg
LIF vs. TRPH	83	9	8
LIF vs. TPH	84	9	6
TPH vs. TRPH	93	2	5

Port Hueneme National Test Site Demo

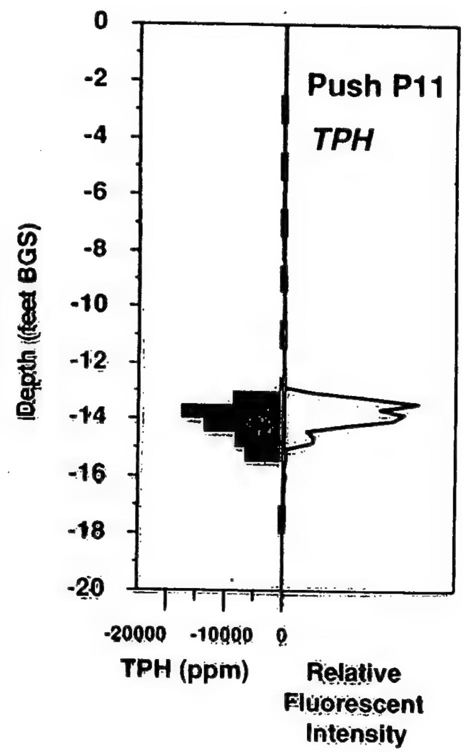


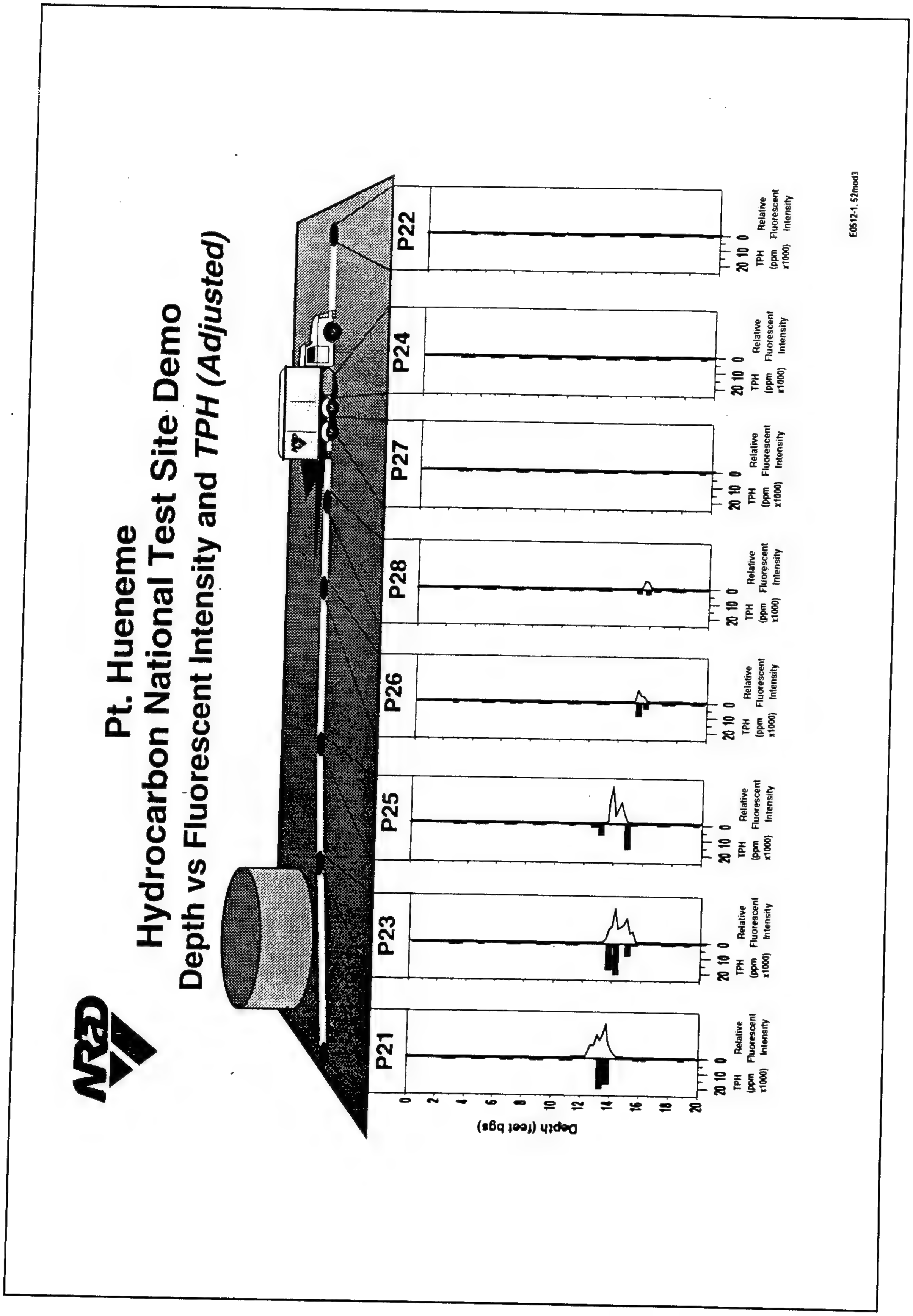
E0611-2.82



Pt. Hueneme
Hydrocarbon National Test Site Demo
Depth vs Fluorescent Intensity
P21
P23
P25
P26
P28
P27
P24
P22
Depth (feet bgs)
0
2
4
6
8
10
12
14
16
18
20
Relative Fluorescent Intensity
E0512-1.52mod2

Depth vs Fluorescent Intensity




Pt. Hueneme
Hydrocarbon National Test Site Demo
Depth vs Fluorescent Intensity and TPH (Adjusted)
P21
P23
P25
P26
P28
P27
P24
P22
Depth (feet bgs)
0 2 4 6 8 10 12 14 16 18 20
20 10 0
TPH (ppm x1000)
Relative Fluorescent Intensity
E0512-1.52mod3

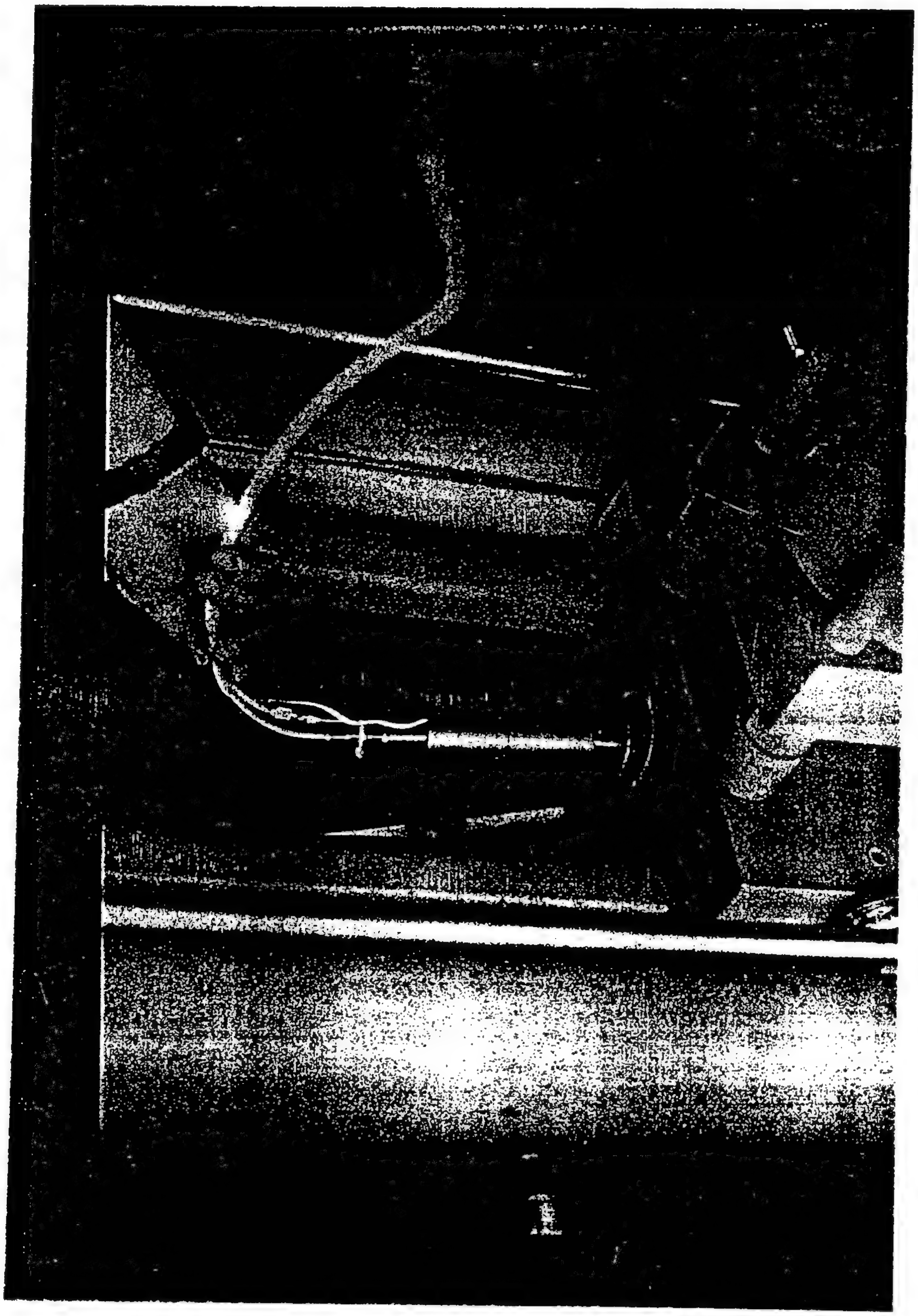
Demonstration of Direct Sparge Volatile Organic Carbon Sampler with Hydropunch Direct Push Groundwater Sampler with the Site Characterization and Analysis Penetrometer System

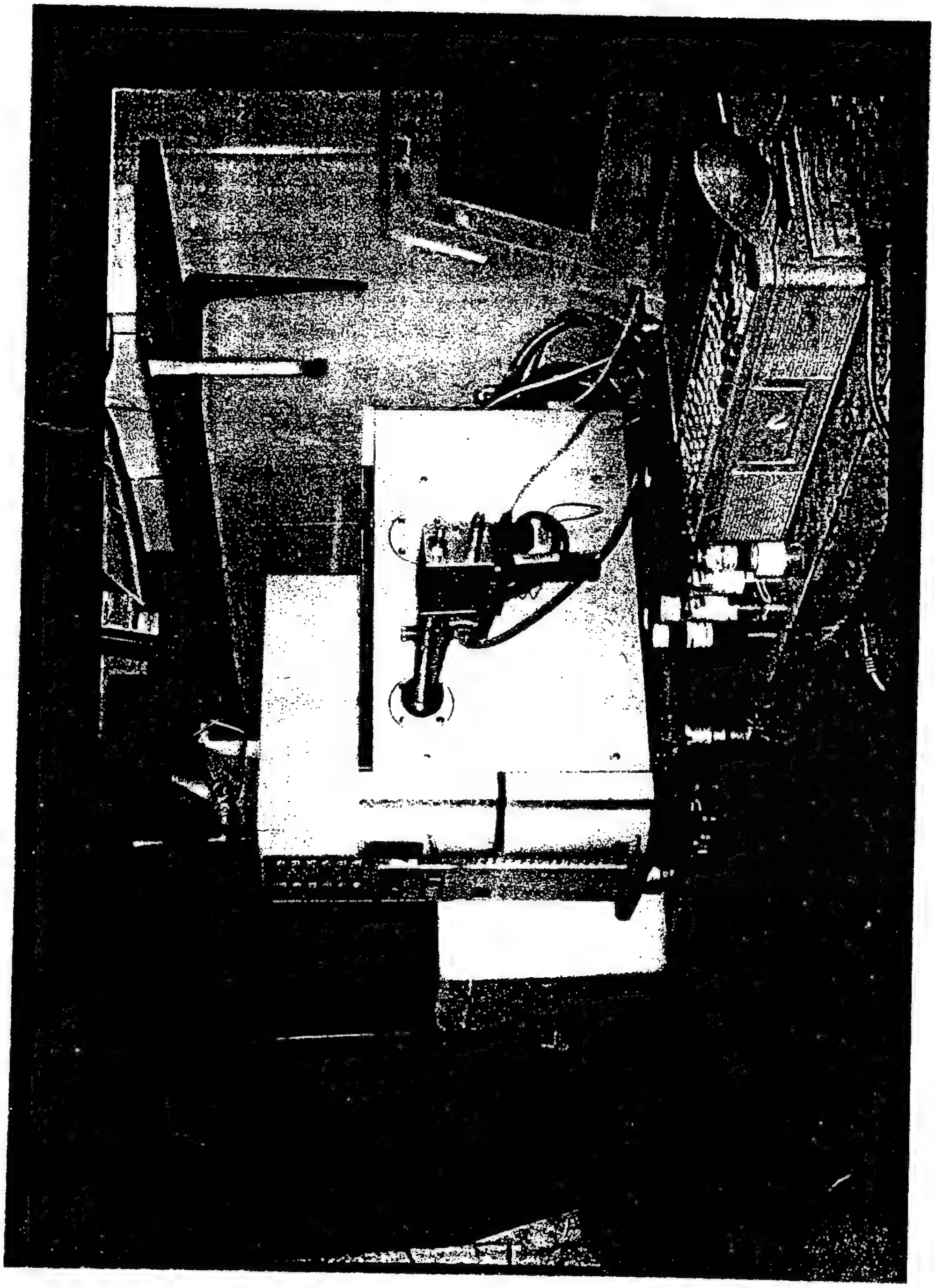
Lead Organization:
U.S. Army Environmental Center
Aberdeen Proving Grounds, MD 21010-5401

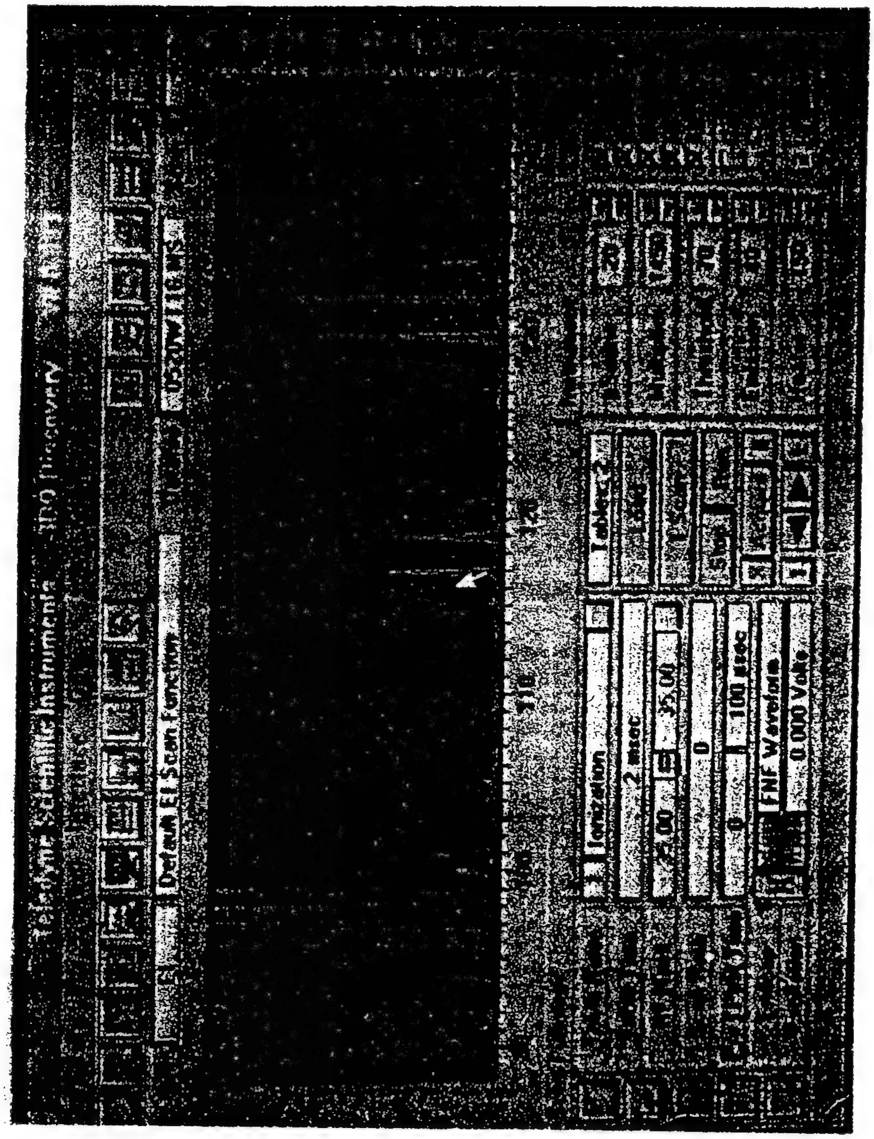
POC: Mr. George Robitaille
SFIM-AEC-ETP
Voice: 410-612-6865
FAX: 410-612-6836

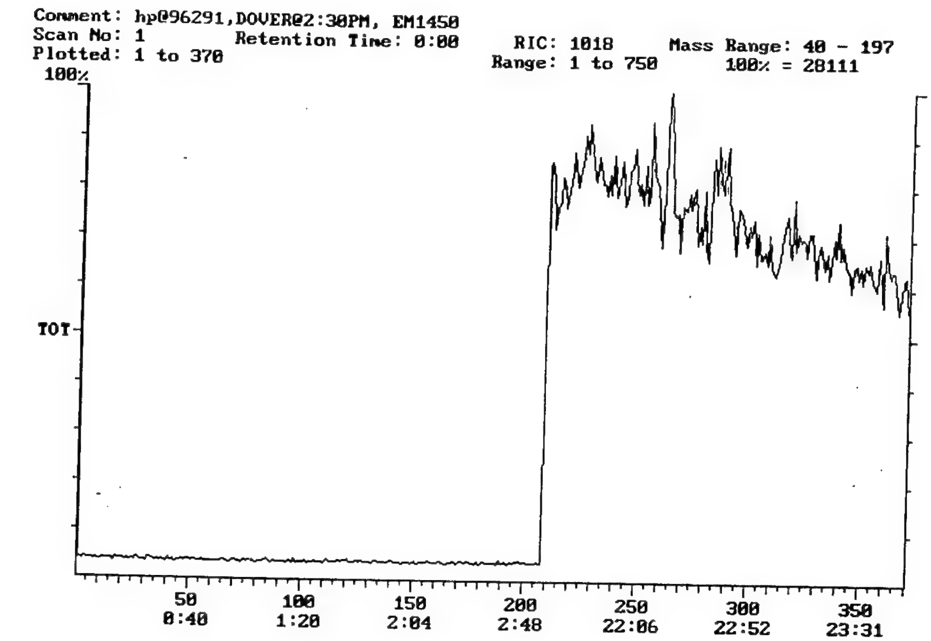
TECHNICAL DESCRIPTION

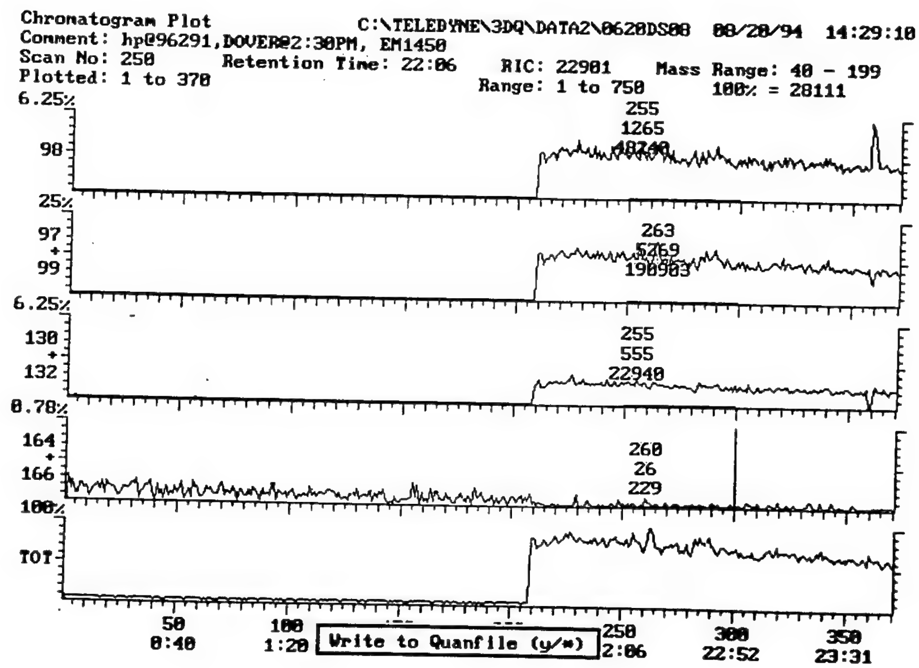
- Hydropunch commercially available direct push groundwater sampler to access groundwater
- Direct sparge sampler strips VOCs from groundwater in-situ and transports analytes to surface
- Analytes identified and quantified using Teledyne field portable ITMS






Default EI Scan Function
Ionization
2 msec
25.00
35.00
100 msec
FNF Waveform
0.000 Volts


Comment: hp096291,DOVER02:30PM, EM1450
Scan No: 1 Retention Time: 0:00
Plotted: 1 to 370
RIC: 1018 Mass Range: 40 - 197
Range: 1 to 750 100% = 28111
100%
TOT
50 0:40
100 1:20
150 2:04
200 2:48
250 22:06
300 22:52
350 23:31

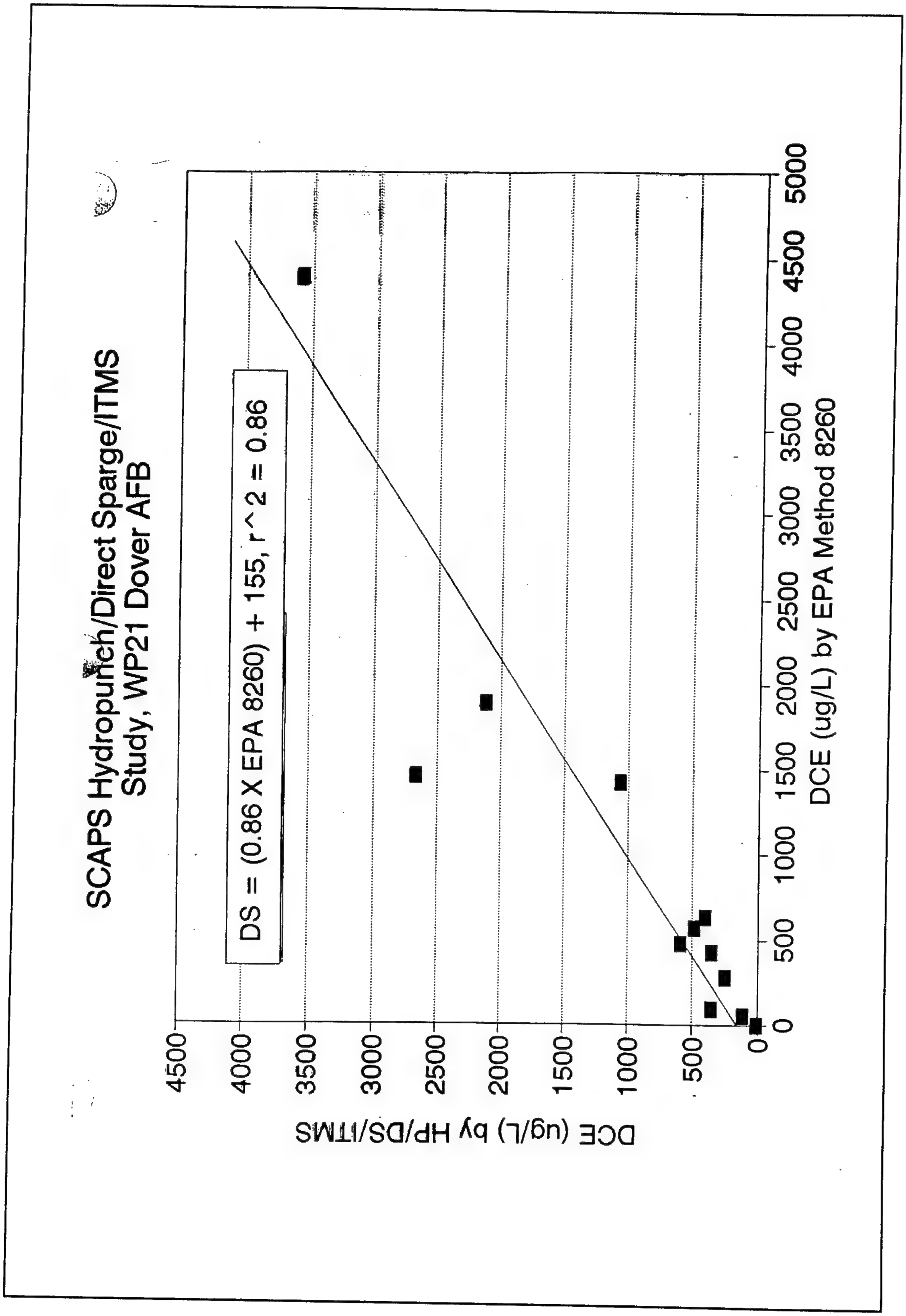

Chromatogram Plot C:\TELEDYNE\3DQ\DATA2\0620DS00 08/20/94 14:29:10
Comment: hp096291,DOVER02:30PM, EM1450
Scan No: 250 Retention Time: 22:06
Plotted: 1 to 370
RIC: 22901 Mass Range: 40 - 199
Range: 1 to 750 100% = 28111
6.25%
98
255
1265
25%
97
+
99
263
190903
6.25%
130
+
132
255
555
22940
0.78%
164
+
166
260
26
229
100%
TOT
50 0:40
100 1:20
Write to Quanfile (y/n)
250 2:06
300 22:52
350 23:31

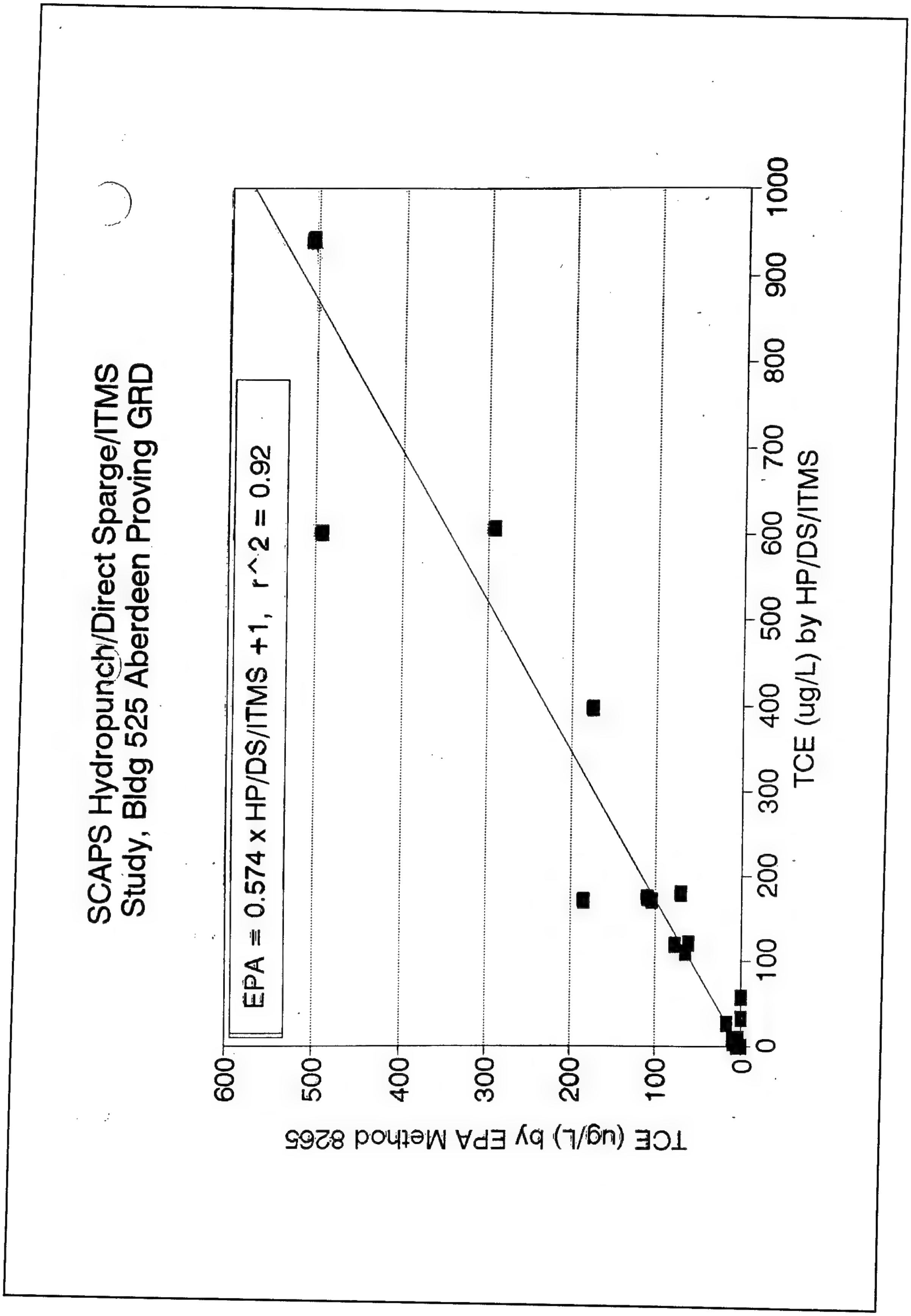
METHOD FOR VERIFYING TECHNOLOGY

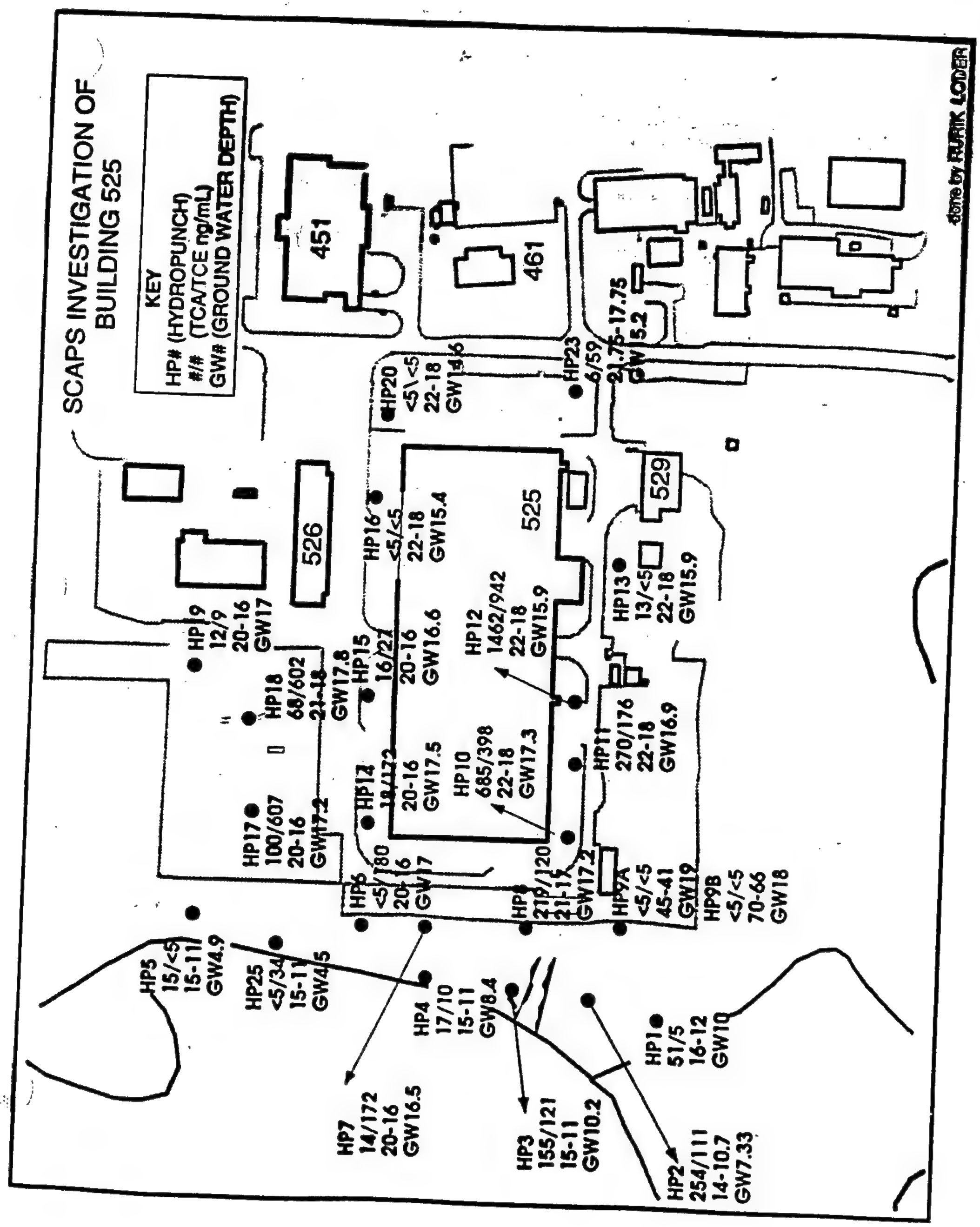
- Obtain groundwater samples from each Hydropunch/direct sparge/ITMS experiment for laboratory analysis by EPA Method 8260
- Compare Hydropunch/direct sparge/ITMS results with data obtained from conventional monitoring wells at each site
- Low flow pumping in place of bailers for collection of samples

PERFORMERS

- AEC, Mr. George Robitaille, SFIM-AEC-ETP, Aberdeen Proving Grounds, MD; Project management, coordination with users and regulators
- WES, Dr. William M. Davis, CEWES-ES-P, 3909 Halls Ferry Road, Vicksburg, MS; conduct field demonstration/validation, laboratory analysis/data reduction, document results in guidance documents
- ORNL, Dr. Mark Wise, Martin Marietta Energy Systems, Inc., ORNL, P.O. Box 2008, Building 4500-S, Oak Ridge, TN; provide support and assistance with field demonstration/ validation, data reduction and documentation


SCAPS Hydropunch/Direct Sparge/ITMS Study, WP21 Dover AFB
DS = (0.86 X EPA 8260) + 155, r^2 = 0.86
DCE (ug/L) by HP/DS/ITMS
DCE (ug/L) by EPA Method 8260
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000


SCAPS Hydropunch/Direct Sparge/ITMS
Study, Bldg 525 Aberdeen Proving GRD
EPA = 0.574 x HP/DS/ITMS +1, r^2 = 0.92
TCE (ug/L) by EPA Method 8265
TCE (ug/L) by HP/DS/ITMS
0
100
200
300
400
500
600
700
800
900
1000


SCAPS INVESTIGATION OF BUILDING 525
KEY
HP# (HYDROPUNCH)
#/# (TCA/TCE ng/mL)
GW# (GROUND WATER DEPTH)
451
461
526
525
529
HP20
HP23
HP19
12/9
20-16
GW17
HP18
68/602
HP15
HP16
<5/<5
22-18
GW15.4
HP12
1462/942
22-18
GW15.9
HP10
685/398
22-18
GW17.3
HP13
13/<5
22-18
GW15.9
HP11
270/176
22-18
GW16.9
HP17
100/607
20-16
HP9B
<5/<5
70-66
GW18
HP5
15/<5
15-11
GW4.9
HP25
HP4
17/10
15-11
GW8.4
HP1
51/5
16-12
HP7
14/172
20-16
GW16.5
HP3
155/121
15-11
GW10.2
HP2
254/111
14-10.7
GW7.33

6 SERDP Peer Review Panel Conclusions and Recommendations

The SERDP funded Tri-Service Accelerated SCAPS Sensor Development Project is composed of seven research areas as follows:

I. Laser Induced Breakdown Spectroscopy (LIBS) sensor development for detecting metals in soils.

II. Laser Induced Fluorescence (LIF) sensor development for detecting
   a. POL contaminants
   b. Explosive contaminanants

III. Fiber Optic Raman Sensor (FORS) development for detecting VOCs (LNAPLS and DNAPLS).

IV. Electrochemical sensors for detecting
   a. Explosive contaminants
   b. VOCs

V. Spectral Gamma probe for detecting radioactive wastes

VI. SCAPS sampler development
   a. Thermal desorption VOC sampler
   b. Multiport sampler

VII. Data processing methodologies to provide on site 3-D visualization and to interface emerging sensors into the SCAPS data acquisition, processing, and visualization systems

The SERDP project briefings were arranged in the order listed above and the briefing materials are included in this chapter. Since some of the research areas are being pursued by multiple Tri-Service partners, some of the research areas contain more than one set of briefing materials.

7 User Needs

SCAPS users from the Army Corps of Engineers Districts, the EPA, and DOE were invited to attend and to participate in the presentations and discussions. Mr. Arbor Drinkwine of the Kansas City District of the Corps of Engineers presented a video describing their innovative over coring technique used to verify SCAPS LIF sensor responses. This technique has been very useful in reducing the effects of soil/contaminant heterogeneities, and for comparing LIF sensor results with EPA approved methods in order to obtain regulatory acceptance of SCAPS technologies. Mr. Bob Lien of the Environmental Protection Agency, Ada OK, presented a slide briefing of a different coring technique that is also applicable to the verification of SCAPS sensor responses. Due to the format of these presentations, no hardcopy materials were available for inclusion in this report.

8 DOE Related Research

A number of DOE and EPA researchers were invited to attend the workshop and to make presentations on their ongoing research that is relevant to the SCAPS sensor development effort. This chapter contains the unedited briefing materials submitted for this portion of the workshop.

On-Line Organic Samplers for the Cone Penetrometer

P.V. Doskey, J.H. Aldstadt, and M.D. Erickson

Environmental Research Division
Argonne National Laboratory

A. Robbat

Chemistry Department
Tufts University

Outline

- Objective
- Approach
- Results
  - *In Situ* Purge Device
  - Thermal Desorption Device
  - Transfer Line
- Conclusions
- FY 96 Plans

Objective

To provide *in situ*, on-line analyses for VOCs and SVOCs in subsurface materials.

- Maintain sample integrity
- Eliminate sample manipulation
- Increase speed of data acquisition
- Decrease the cost of site characterizations

Approach

In Situ Purging

In Situ Thermal Desorption

Transfer Line

Prescreening with non-destructive detector

Preconcentration

Detection and Quantitation - GC/MS

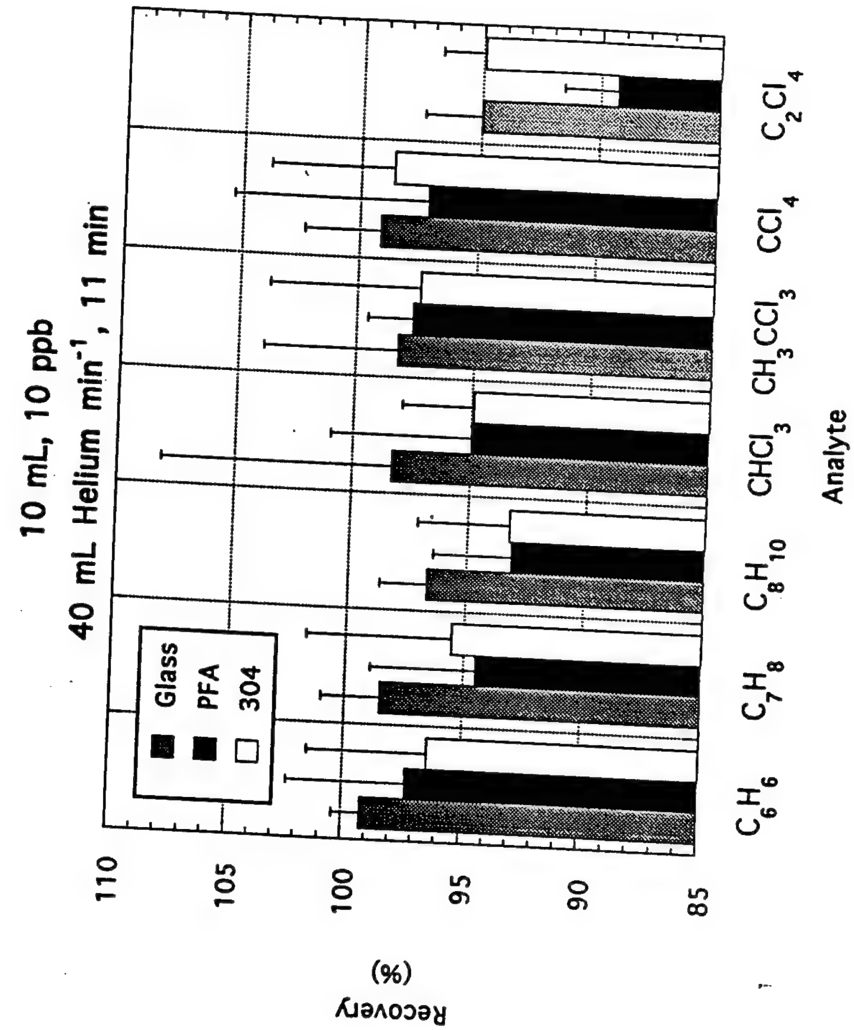
In Situ Purge Device Materials

Type 304 Stainless Steel

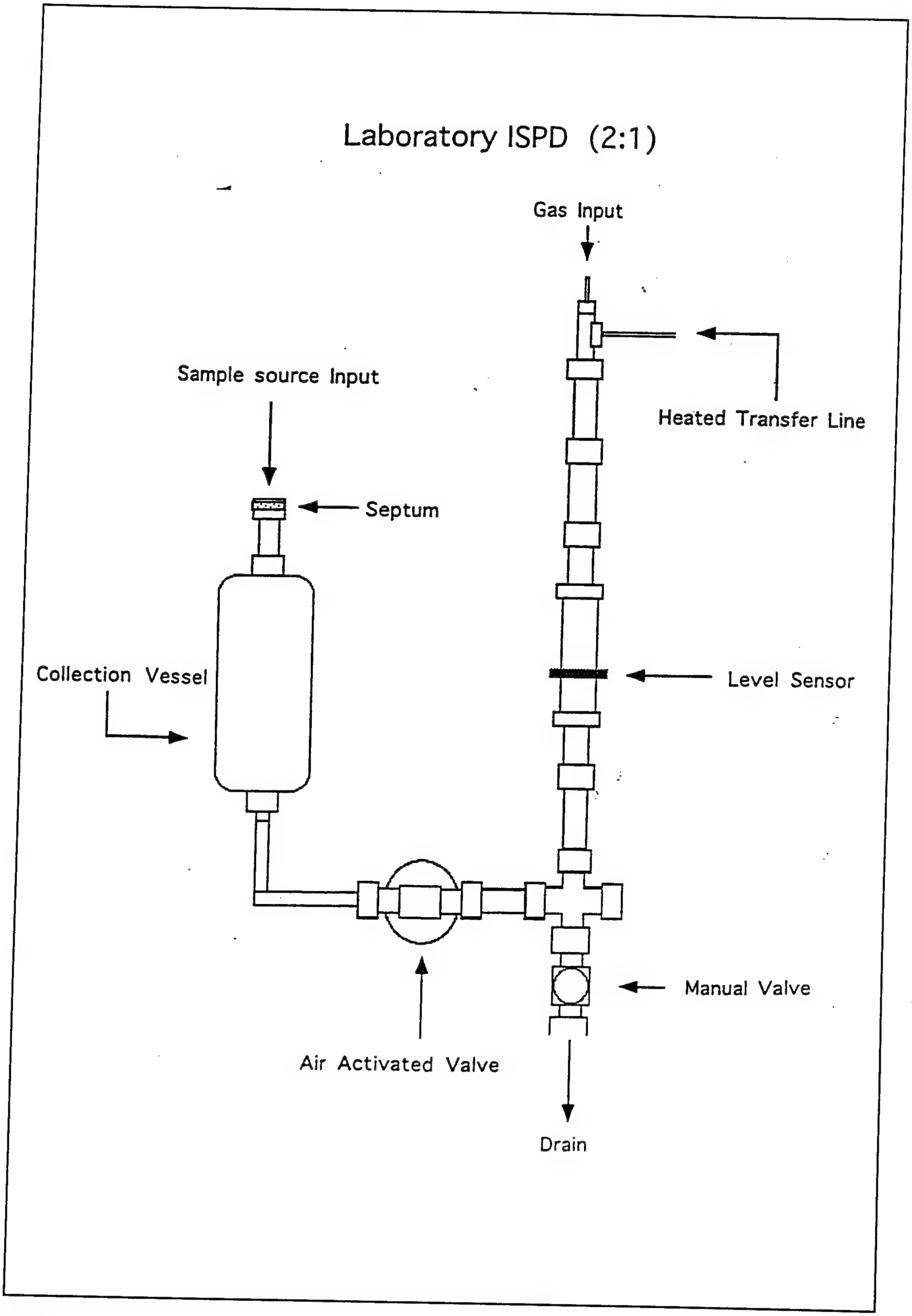
- 75 mL Gas Sampling Cylinder

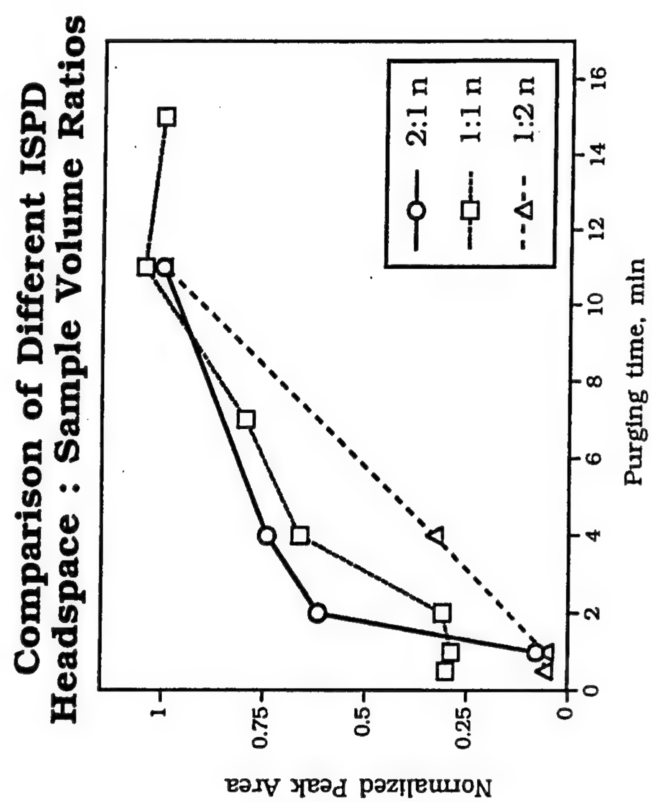
Teflon®PFA

- 2.667 cm OD Pipe

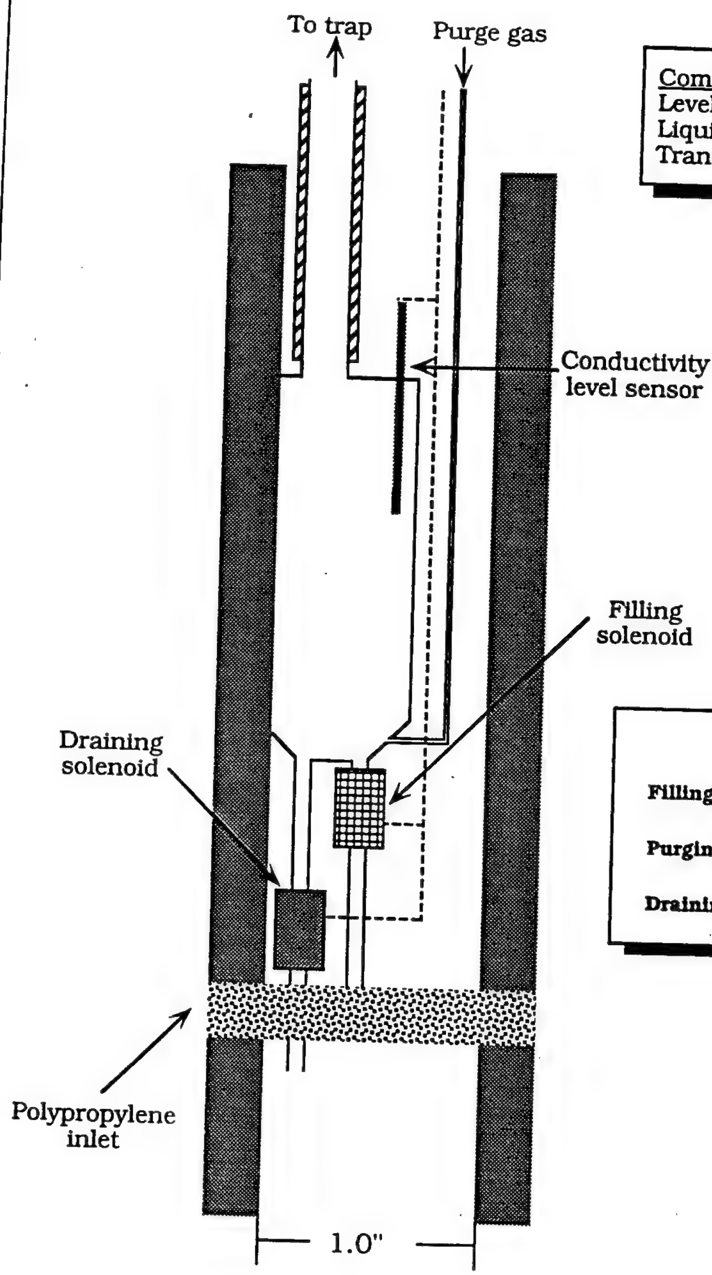


10 mL, 10 ppb
40 mL Helium min^{-1}, 11 min
Glass
PFA
304
Recovery (%)
110
105
100
95
90
85
C_6H_6
C_7H_8
C_8H_{10}
$CHCl_3$
CH_3CCl_3
CCl_4
C_2Cl_4
Analyte


Laboratory ISPD (2:1)
Gas Input
Sample source Input
Heated Transfer Line
Septum
Collection Vessel
Level Sensor
Manual Valve
Air Activated Valve
Drain


Comparison of Different ISPD
Headspace : Sample Volume Ratios
Normalized Peak Area
0
0.25
0.5
0.75
1
0
2
4
6
8
10
12
14
16
Purging time, min
2:1 n
1:1 n
1:2 n

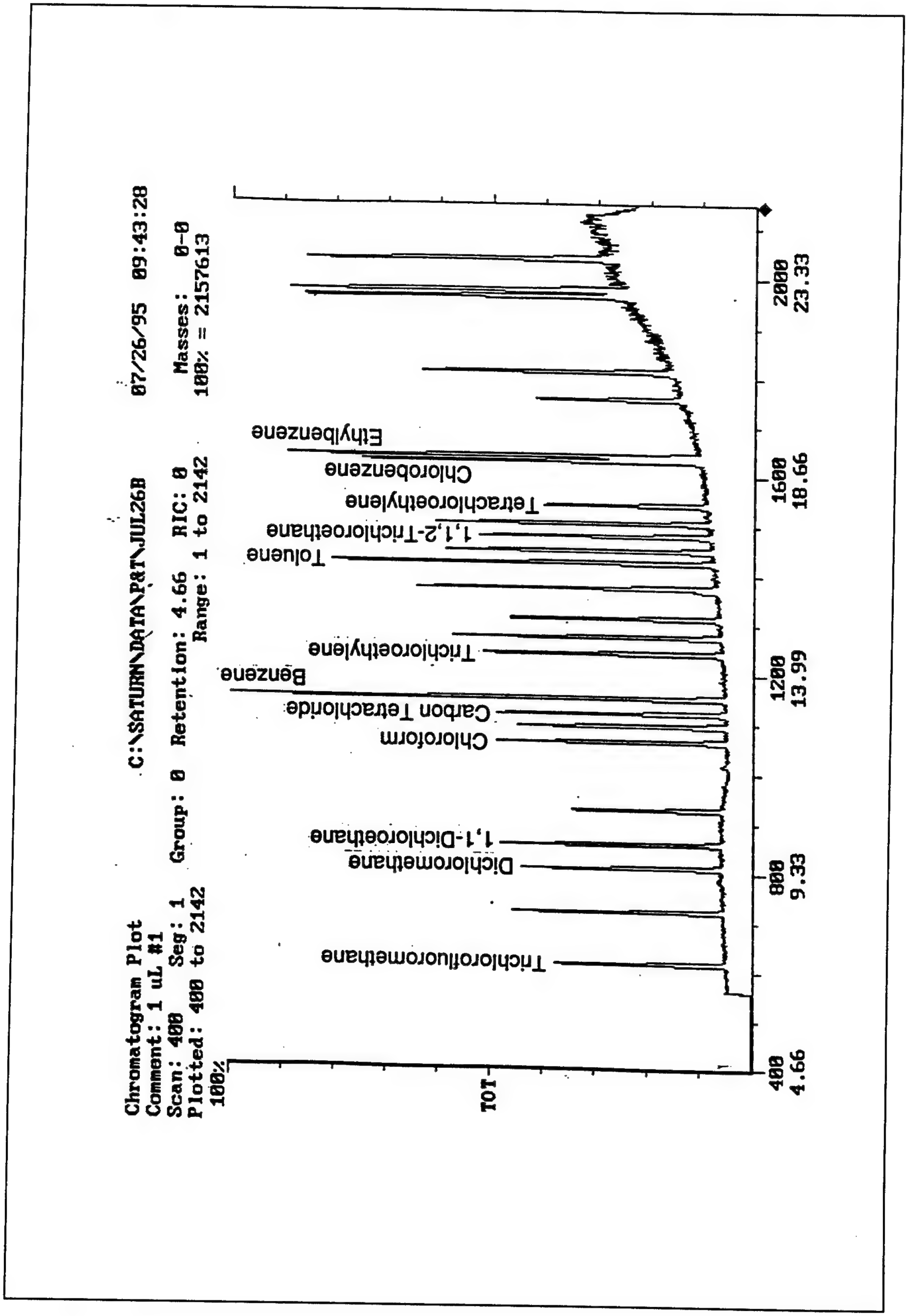
Schematic of ISPD



Component:	Supplier:
Level Sensor	Pepperl+Fuchs
Liquid Valves	Asco
Transfer Line	Parflex

- - - - electrical wiring

	Fill Valve	*Drain Valve*
Filling	Open	Closed
Purging	Closed	Closed
Draining	Closed	Open


Chromatogram Plot
Comment: 1 uL #1
Scan: 400 Seg: 1
Plotted: 400 to 2142
C:\SATURN\DATA\P&T\JUL26B
Group: 0 Retention: 4.66 RIC: 0
Range: 1 to 2142
07/26/95 09:43:28
Masses: 0-0
100% = 2157613
100%
TOT
400
4.66
800
9.33
1200
13.99
1600
18.66
2000
23.33
Trichlorofluoromethane
Dichloromethane
1,1-Dichloroethane
Chloroform
Carbon Tetrachloride
Benzene
Trichloroethylene
Toluene
1,1,2-Trichloroethane
Tetrachloroethylene
Chlorobenzene
Ethylbenzene

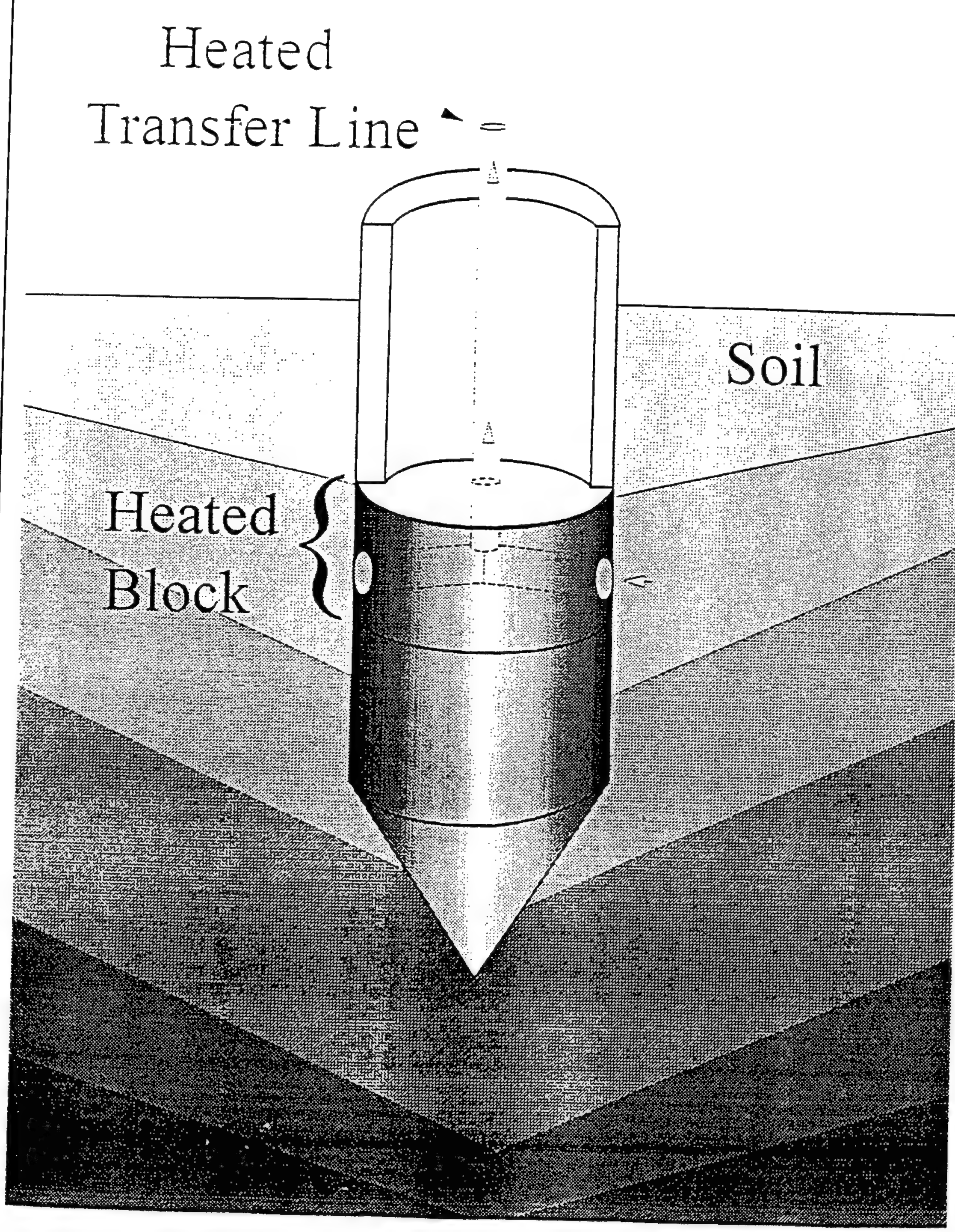
Conclusions

In Situ Purge Device

Sparging efficiencies for vessels made of glass, Teflon®, and stainless steel are similar.

The optimum headspace to sample volume ratio for a purge vessel is 2:1.

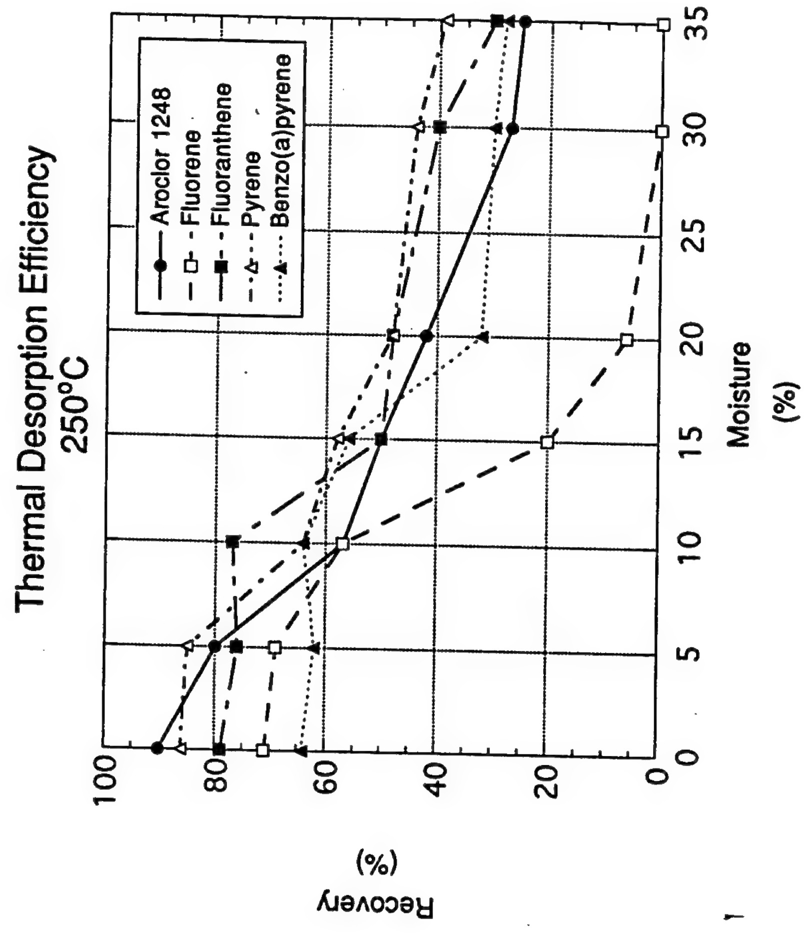
A stainless steel ISPD has been integrated within a CPT push rod that employs microvalve technology and a conductivity level sensor to accurately purge a 5 mL groundwater sample as described in EPA Method 624.


Heated
Transfer Line
Soil
Heated
Block

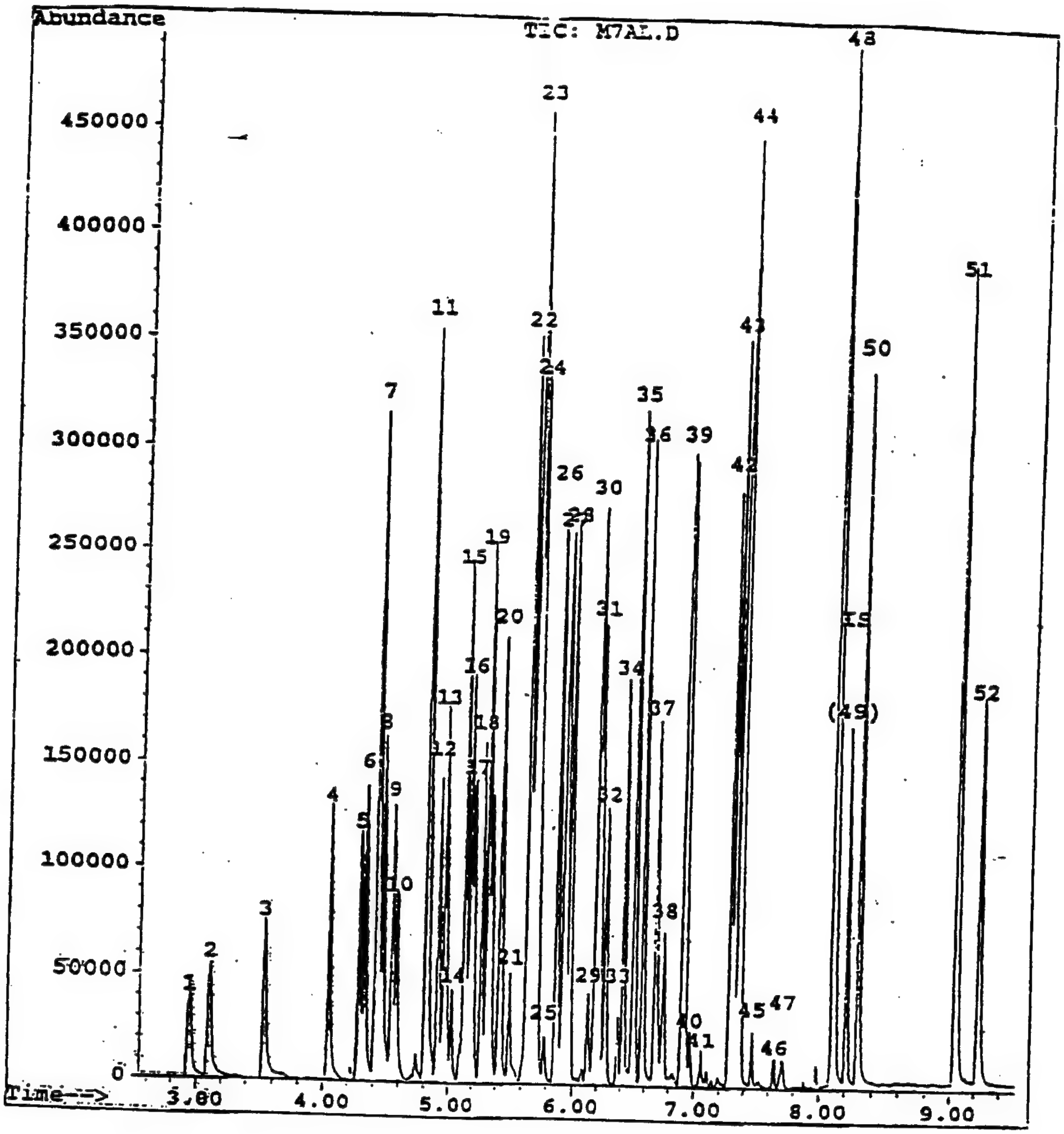
Material Balance for Standard Addition to Dry Sand

Analyte	Transferred (%)		Residual in Soil (%)		Residual in Transfer Line (%)	
	250°C	300°C	250°C	300°C	250°C	300°C
Aroclor 1248	92.4	95.2	5.03	3.10	2.23	0.31
BHC	87.1	91.0	12.0	6.80	0.00	0.00
Dieldrin	73.1	66.0	26.0	18.6	0.50	2.30
4,4'-DDT	67.3	72.3	19.1	13.4	4.50	2.20
Fluorene	71.5	75.4	0.00	2.82	1.95	0.63
Fluoranthene	79.0	80.2	4.50	4.40	3.40	2.68
Pyrene	86.3	82.9	9.00	6.21	1.59	1.40
Benzo[illegible]yrene	64.5	65.4	31.0	23.1	3.90	2.50

28 ppm
12 ppm
15 ppm



Thermal Desorption Efficiency
250°C
Aroclor 1248
Fluorene
Fluoranthene
Pyrene
Benzo(a)pyrene
Recovery
(%)
Moisture
(%)
0
20
40
60
80
100
0
5
10
15
20
25
30
35



Abundance
TIC: M7AL.D
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
Time-->
3.00
4.00
5.00
6.00
7.00
8.00
9.00

Instrument Calibration

Analyte	Dynamic Range (ng)	Detection Limit (ng)	RSTD (%)
α-BHC	0.5 - 1000	0.5	6
PCB (Cl-4)	3.7 - 950	4.0	8
Fluoranthene	0.5 - 1000	0.7	18
Pyrene	0.5 - 1000	1.3	25
Dieldrin	0.5 - 1000	0.7	13
4,4'-DDT	0.5 - 1000	0.5	11
Dibenz[a,h]anthracene	0.5 - 1000	0.6	14

Conclusions

In Situ Thermal Desorption Device

A temperature of 250°C is sufficient to thermally desorb PCBs, PAHs, and pesticides from a dry sample matrix with 50-95% efficiency.

Volumetric flow rates of 15 - 60 mL min^{-1} and purge volumes exceeding at least 30 volumes of the thermal desorption system are necessary to efficiently transfer the desorbed analytes and preconcentrate them on glass wool at -60°C.

The thermal desorption efficiency decreases with increasing water content of the matrix.

Transfer Line Materials

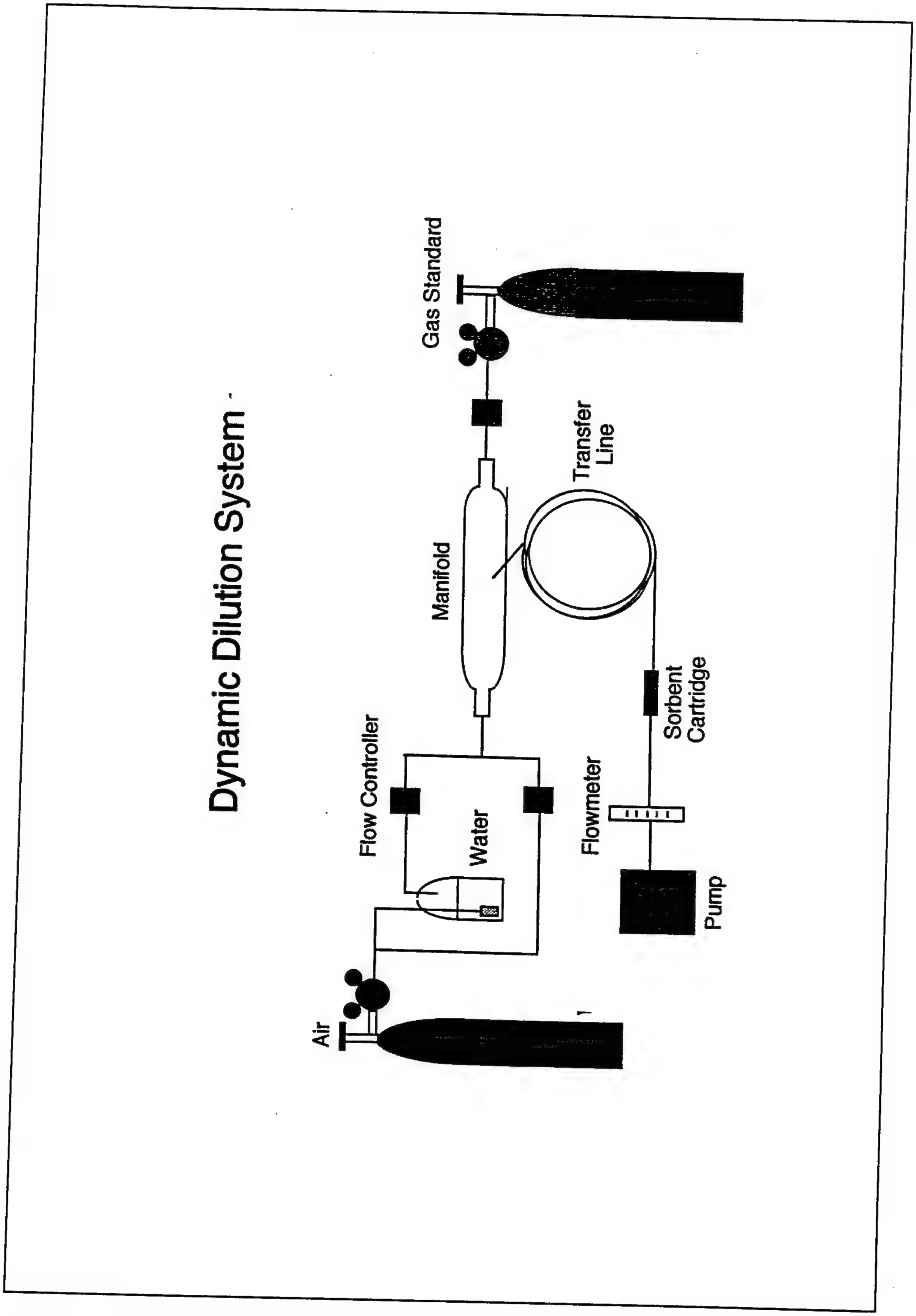
(15 m x 0.318 cm OD x 0.160-0.216 cm ID)

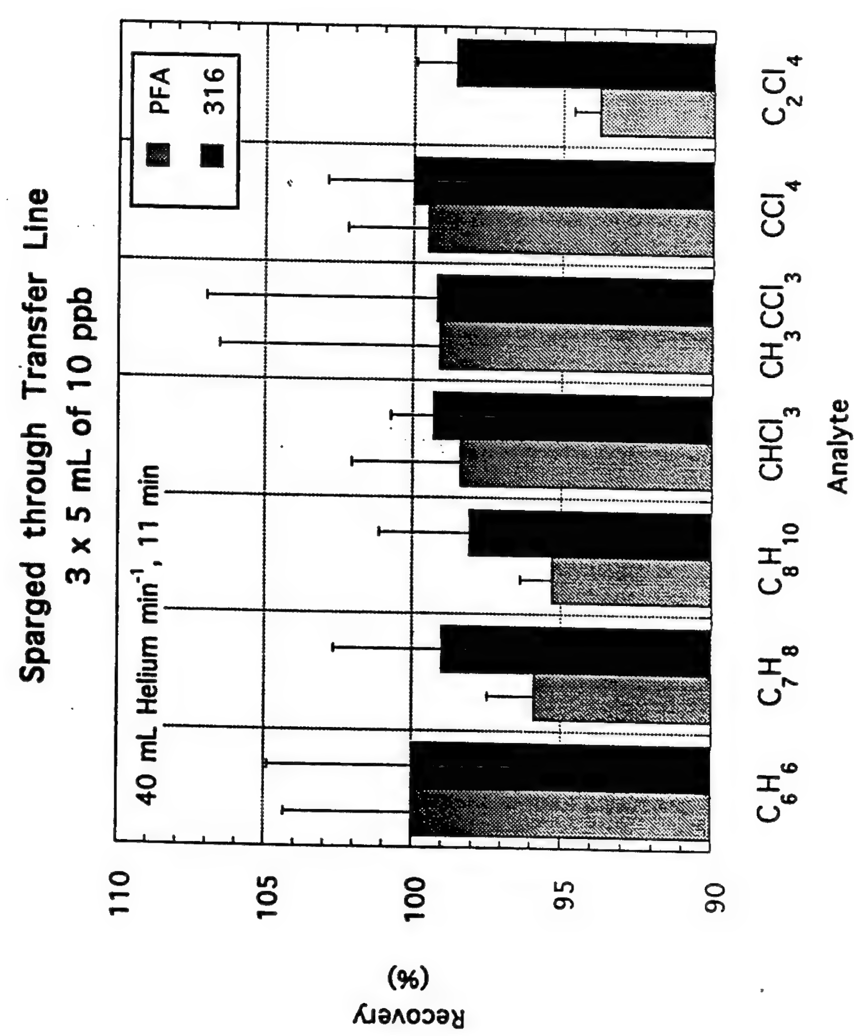
Stainless Steel (Type 304 and Type 316)

Nickel (Type 200)

Aluminum

Teflon® (Type PTFE, FEP, PFA)


Dynamic Dilution System
Gas Standard
Transfer
Line
Manifold
Sorbent
Cartridge
Flow Controller
Flowmeter
Water
Pump
Air


Sparged through Transfer Line
3 x 5 mL of 10 ppb
40 mL Helium min-1, 11 min
PFA
316
Recovery (%)
110
105
100
95
90
C6H6
C7H8
C8H10
CHCl3
CH3CCl3
CCl4
C2Cl4
Analyte

Conclusions

Transfer Line

Stainless steel is superior to Teflon® as a transfer line material.

Gentle heating to prevent condensation of water in the transfer line will be necessary for efficient VOC transfer.

Glass-Lined or passivated stainless steel tubing may be necessary to efficiently transfer SVOCs from the thermal desorption device.

FY 96 Plans

Field test of on-line organic samplers at ANL.	10/95 - 11/95
Laboratory Test of Thermal Desorption Device for VOCs.	10/95 - 11/95
Modify samplers.	12/95 - 2/96
Field tests of on-line organic samplers at additional sites.	3/96 - 8/96

Acknowledgment

Charles H. Batson
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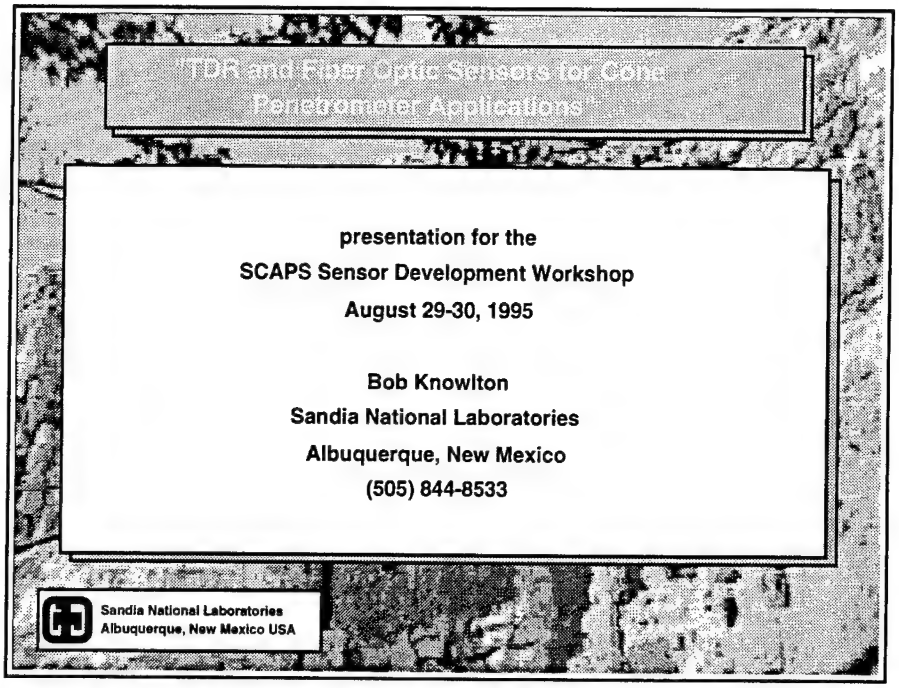
Tammi R. James
Jacqueline M. Kuo
Alice F. Martin

U.S. Department of Energy
Characterization, Monitoring, and Sensor Technology Integrated Program
Office ·' Technology Development

'anager: Caroline Purdy
'ager: Eric Lightner



"TDR and Fiber Optic Sensors for Cone Penetrometer Applications"
presentation for the
SCAPS Sensor Development Workshop
August 29-30, 1995
Bob Knowlton
Sandia National Laboratories
Albuquerque, New Mexico
(505) 844-8533
Sandia National Laboratories
Albuquerque, New Mexico USA

Sponsors
• US Department of Energy
Development (EM-50)
Sandia National Laboratories
Albuquerque, New Mexico USA

Commercial Partners

- **GEOCENTERS, Inc., Boston, Mass. USA**
  - Contributed the fiber optic pore pressure sensor
- **Applied Research Associates, Inc., South Royalton, VT USA**
  - Fabricated and field tested the Sandia probes

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Topics to Cover

- **Objective and needs of research**
- **Design and testing specifications for moisture probe**
- **Design and testing specifications for capillary pore pressure probe**
- **Field testing results**

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Objective:

To design, fabricate, test & evaluate a new cone penetrometer application for characterizing hydrogeologic parameters (with a Time Domain Reflectometry [TDR] sensor and fiber optic probe)

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Data Needs:

- Hydrologic characterization
  - Moisture content and pore pressure are critical parameters for flow & transport modeling (used in risk assessments)
  - Moisture content and pore pressure can be used with stratigraphic info to correlate geologic units
- Remediation
  - Moisture content is important data for optimizing soil vapor extraction options, because volatiles flow readily through low-moisture content, high permeability zones, and not through high-moisture content, low permeability zones
  - Moisture content is important data for optimizing/monitoring bioremediation projects

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TDR Probe

Strong contrast between dielectric of soil (2 to 4) and water (80).
Calculate the dielectric constant of a porous media, Ka:

$$K_a = [l_a / (l_p * v_p)]^2$$

where:

- l_p = actual probe rod length [L]
- l_a = apparent length of the probe rod as determined from the TDR trace [L]
- v_p = propagation velocity of the signal [L/T]

and moisture content is calculated as:

$$\theta_v = -0.053 + (0.0292)K_a - (5.5 \times 10^{-4})K_a^2 + (4.3 \times 10^{-6})K_a^3$$

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TDR Probe (continued)

- For good accuracy, recommend calibrating to the soils at the site
- For precision, expect ± 1% moisture by volume (if calibrated)
- The probe configuration will be of use in two applications:
  - As part of a cone penetrometer sensor system
  - As a down-hole logging device for characterization and post-closure monitoring (a side benefit of this research)

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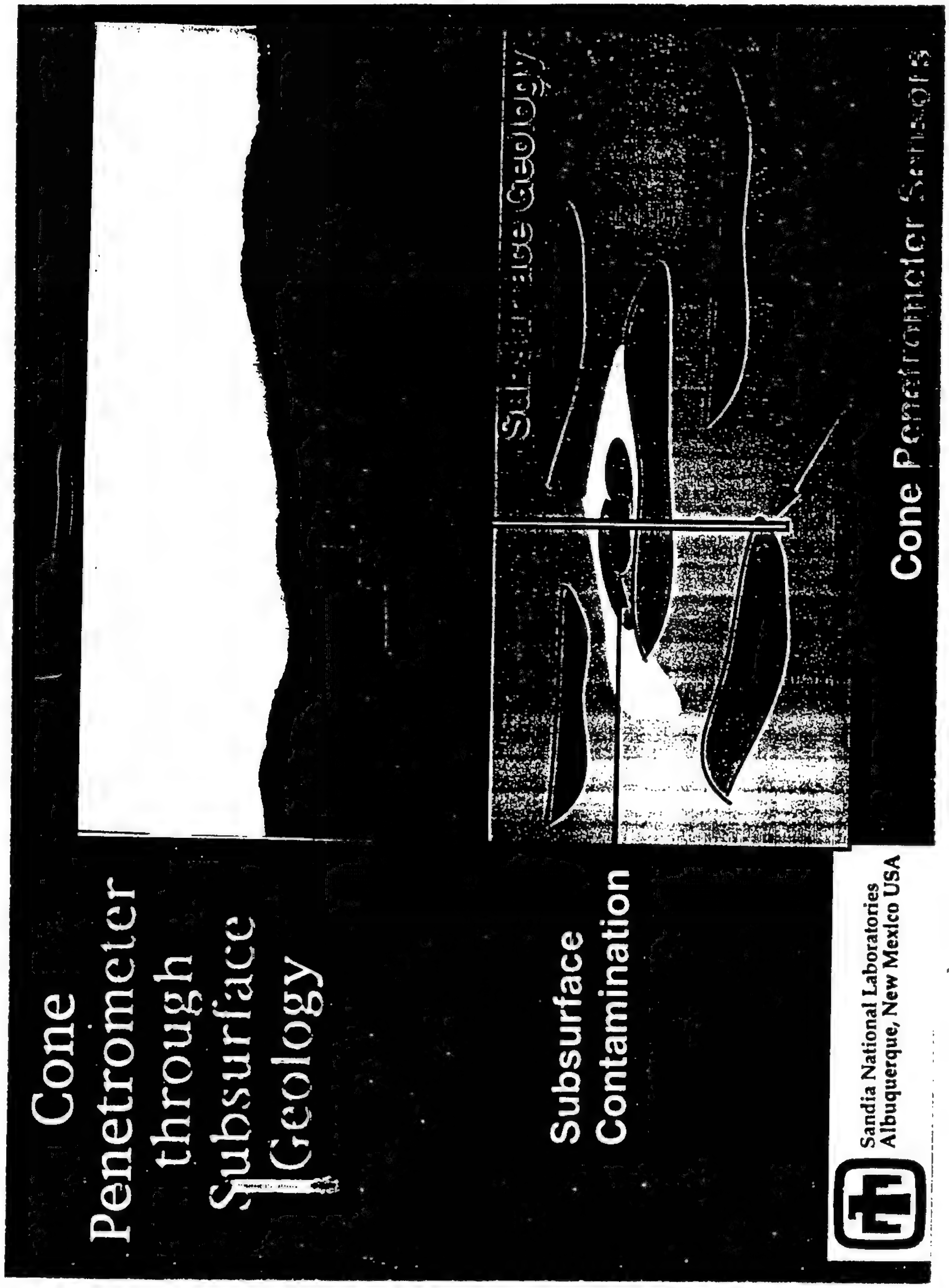
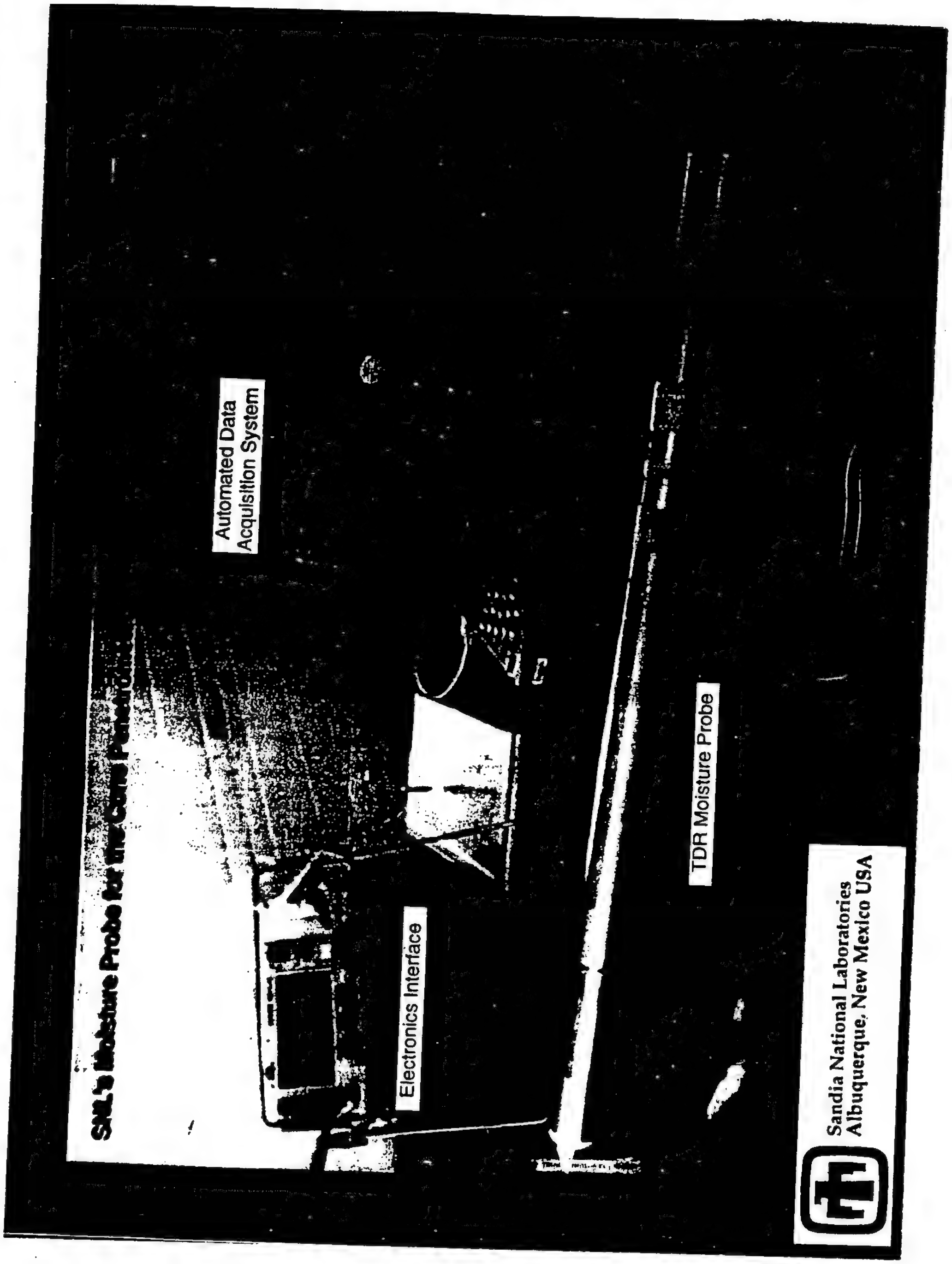
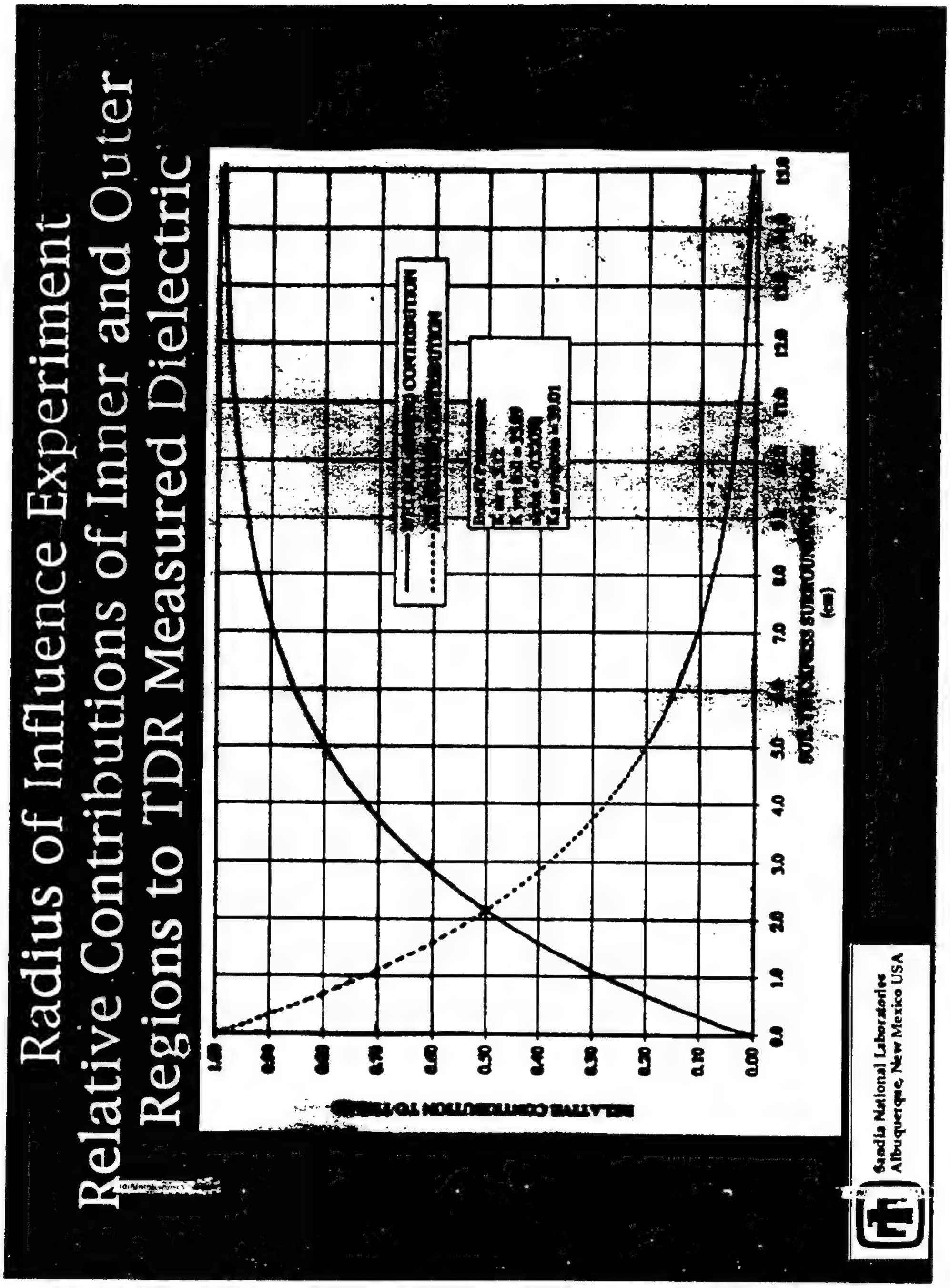
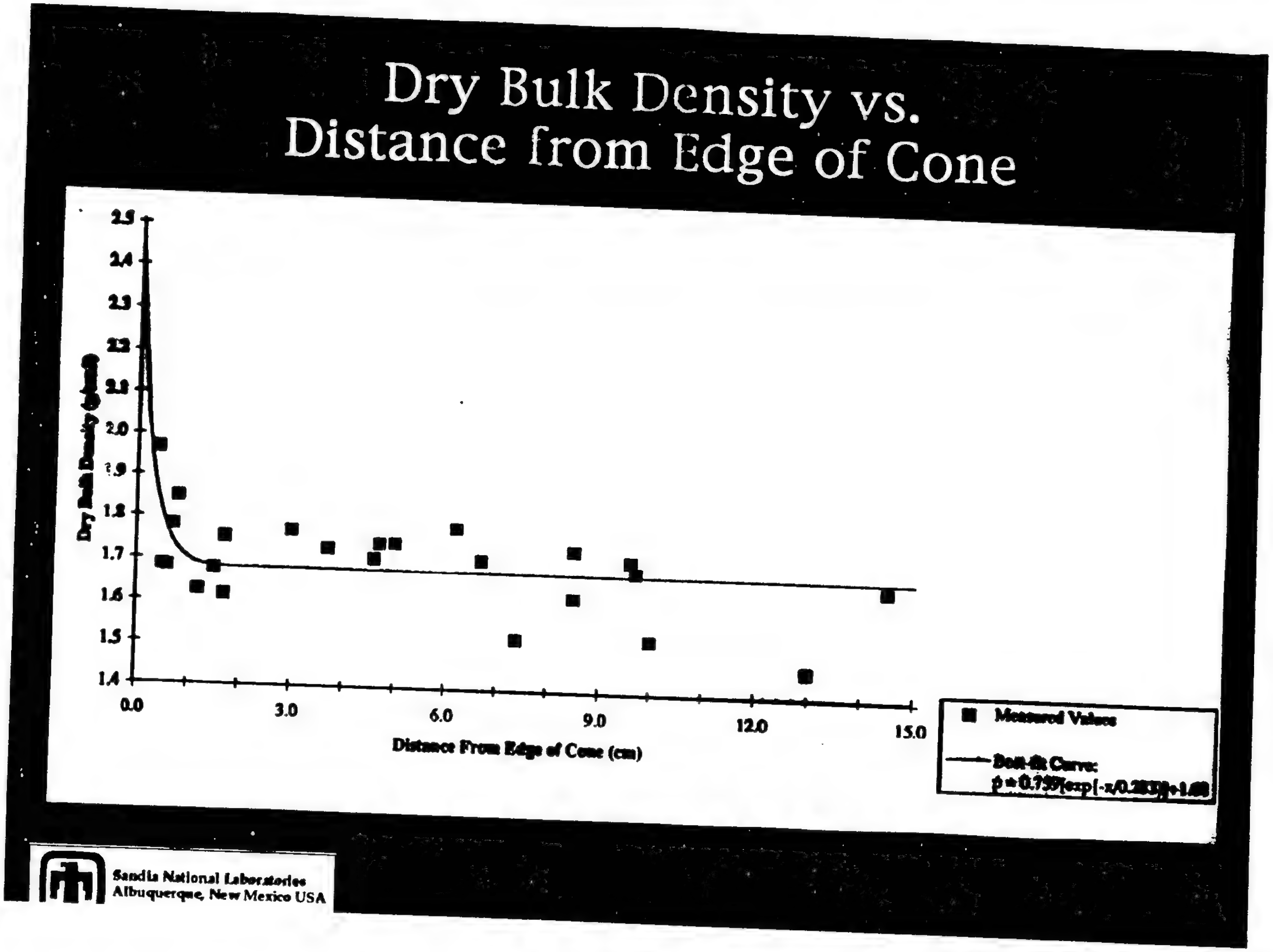

Cone Penetrometer through Subsurface Geology
Subsurface Contamination
Cone Penetrometer Sensors
Sandia National Laboratories
Albuquerque, New Mexico USA


SNL's Moisture Probe for the Cone
Automated Data Acquisition System
Electronics Interface
TDR Moisture Probe
Sandia National Laboratories
Albuquerque, New Mexico USA


Radius of Influence Experiment
Relative Contributions of Inner and Outer
Regions to TDR Measured Dielectric
Sandia National Laboratories
Albuquerque, New Mexico USA


Dry Bulk Density vs.
Distance from Edge of Cone
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
0.0
3.0
6.0
9.0
12.0
15.0
Distance From Edge of Cone (cm)
Measured Values
Best-fit Curve:
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Fiber Optic Capillary Pore Pressure Sensor

- Optical chemical indicator sensor with a porous polymer substrate (patented proprietary product by GEOCENTERS, Inc.), LED dual wavelength optical signal, and a photo-diode/timing circuit to read results.
- The polymer matrix is based on a mixture of:
  - cobalt chloride hexahydrate, and
  - poly-methyl methacrylate (PMMA)
- Measures relative humidity in soil gas, from which capillary pore pressure is calculated: $P_w = (RT/M) \ln (p/p_0) = (RT/M) \ln$ (R.H.)

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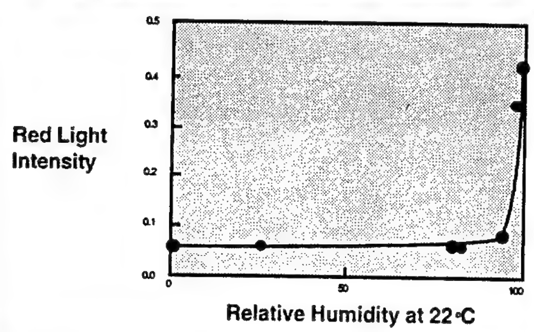
Hydrophobic porous polymer R.H. measurements



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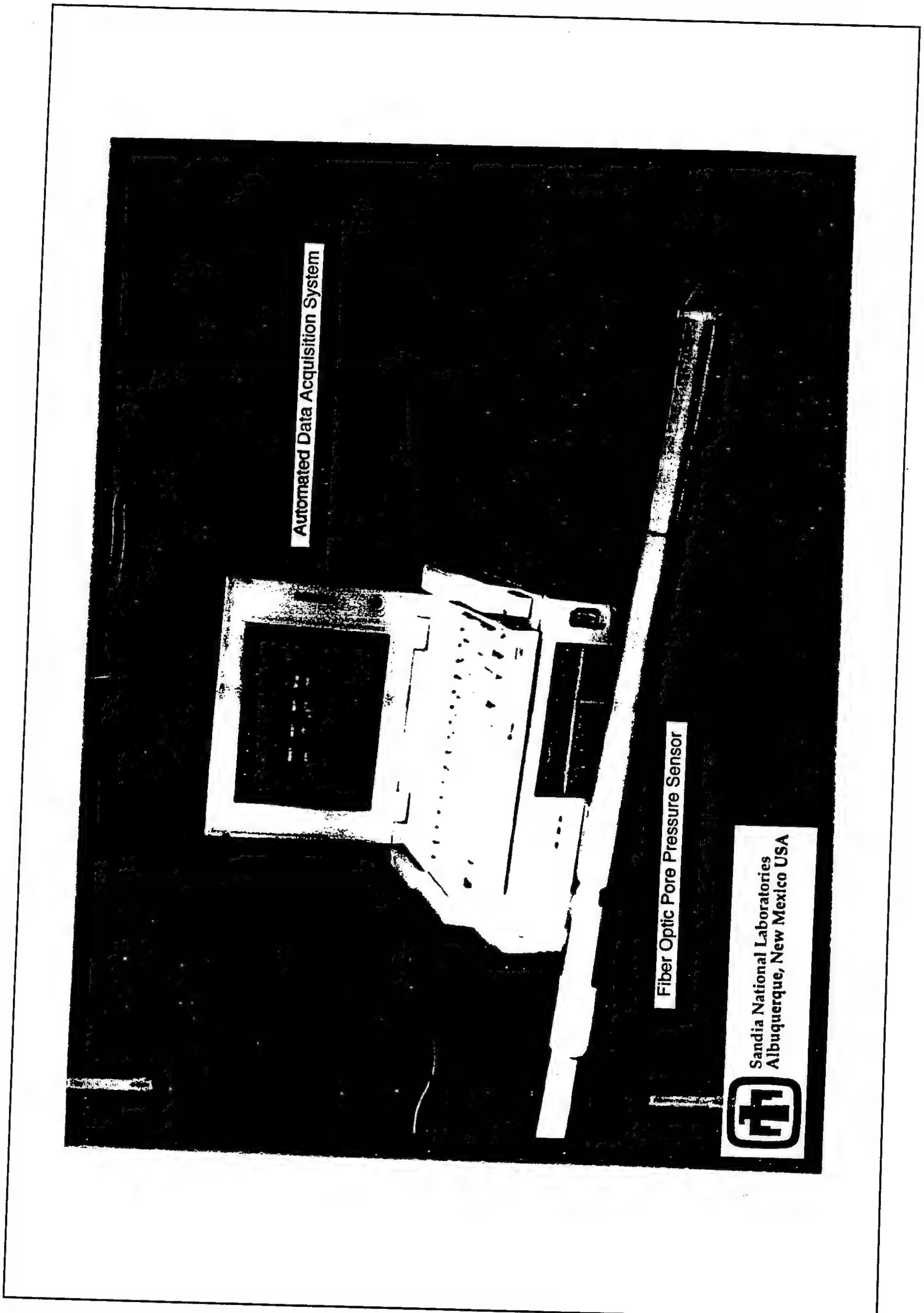
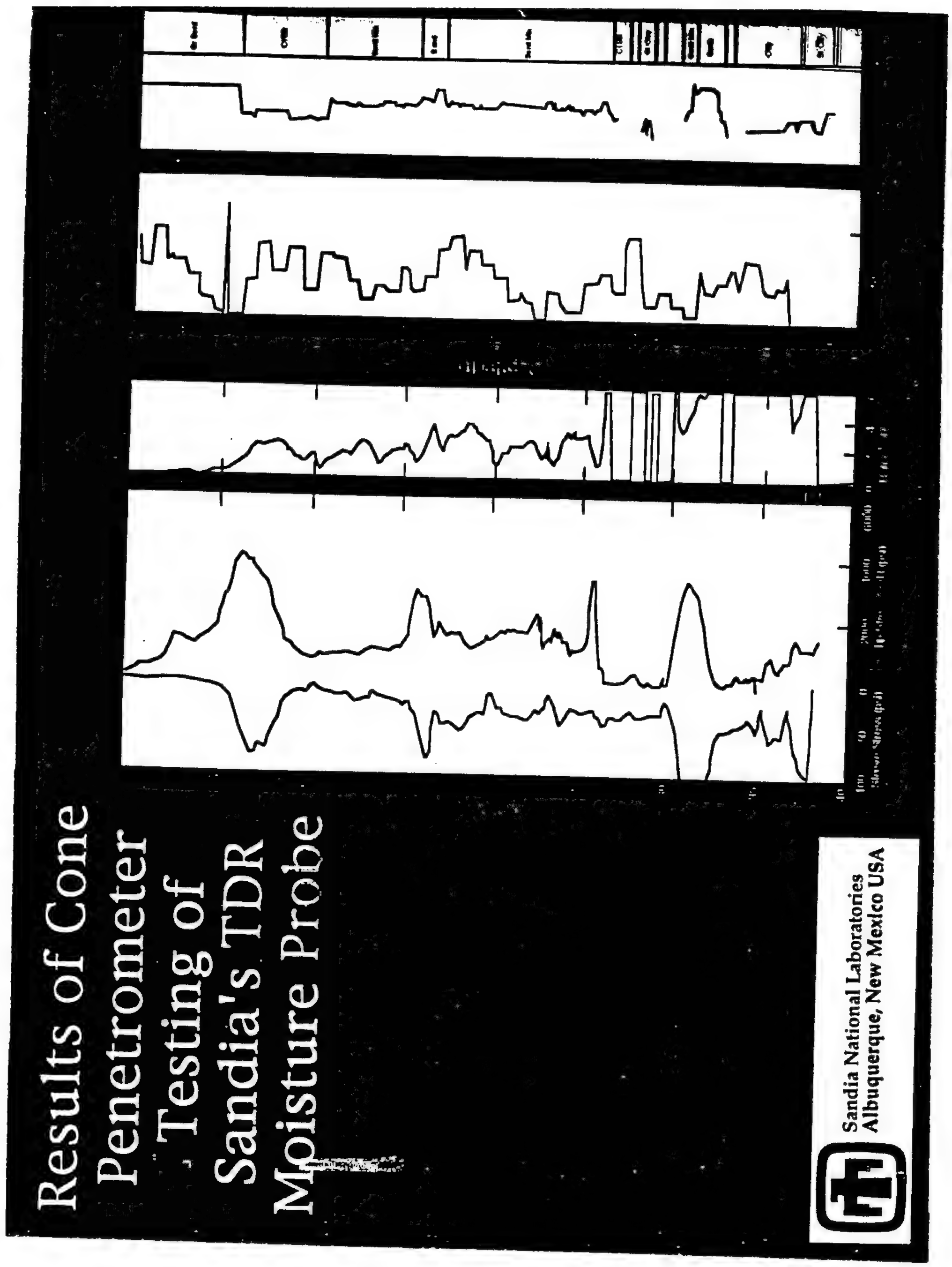
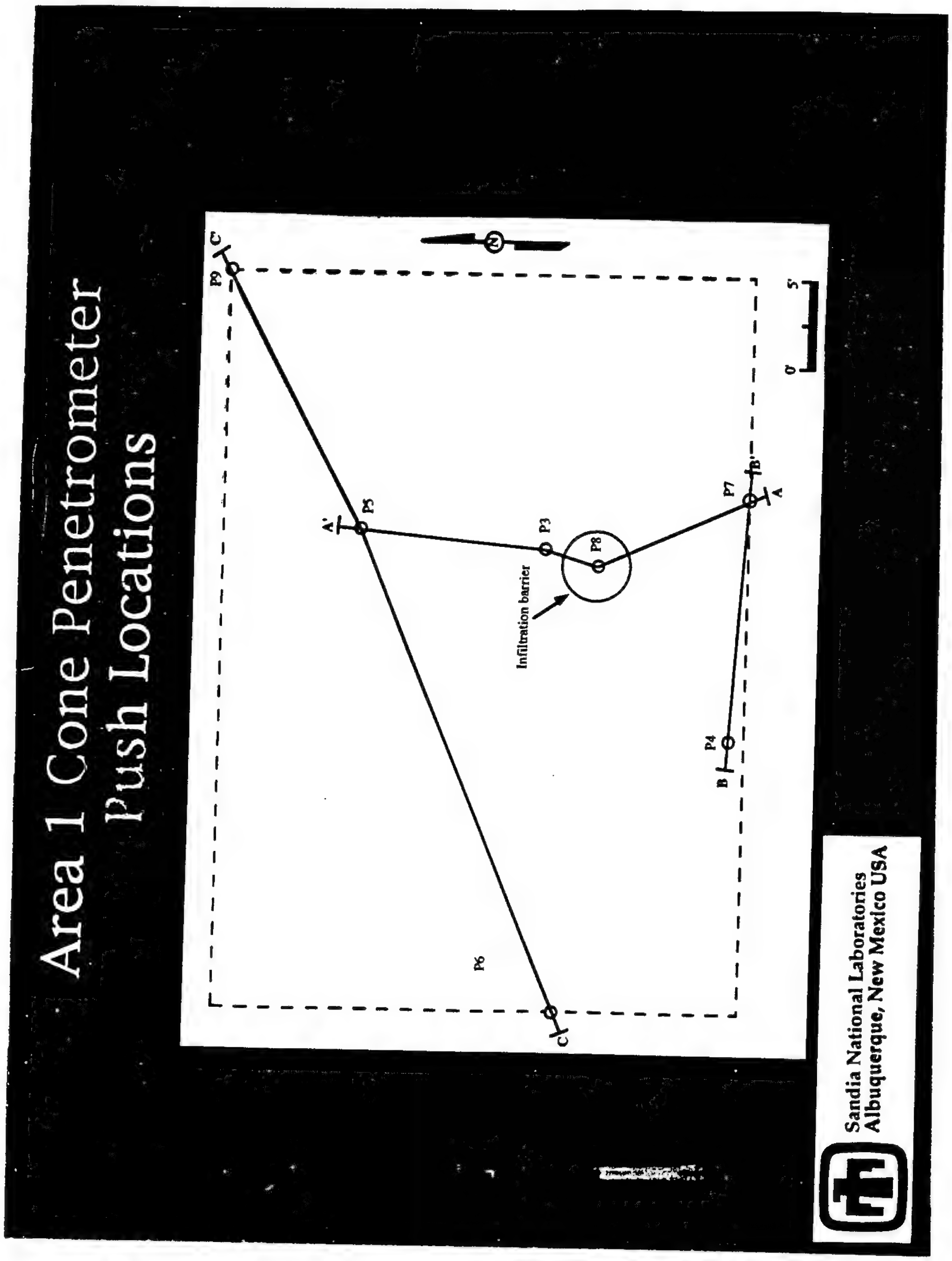
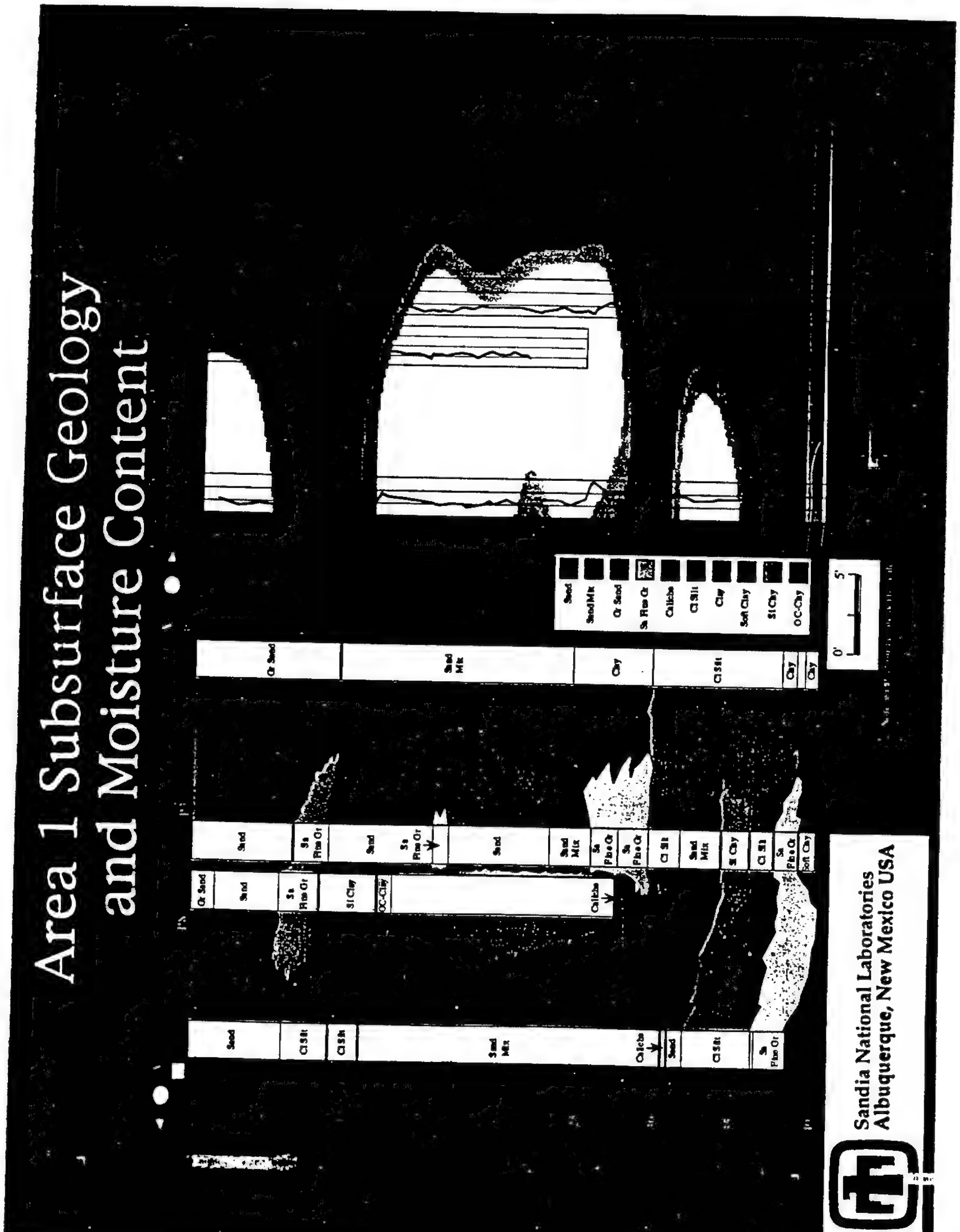
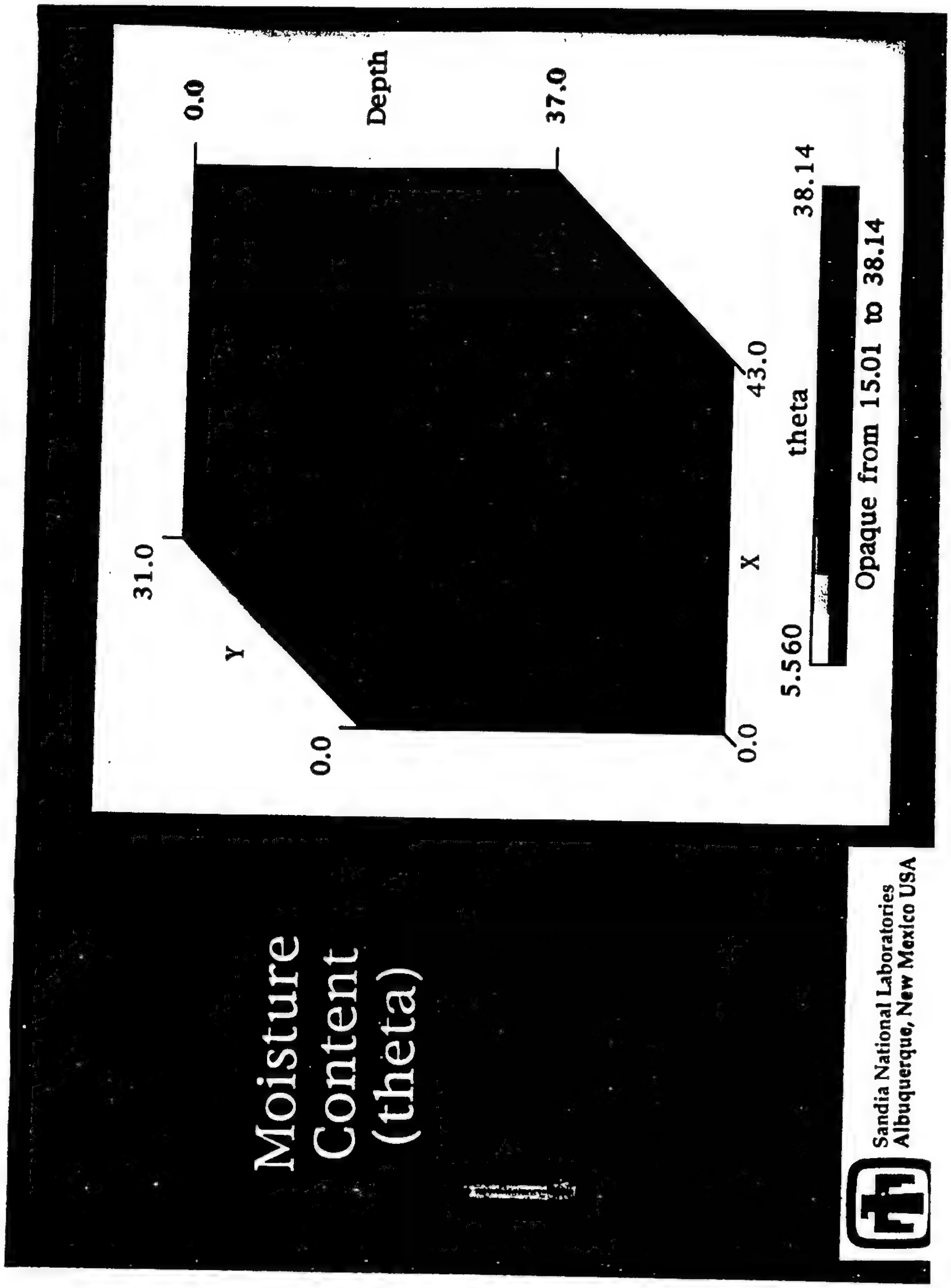

Automated Data Acquisition System
Fiber Optic Pore Pressure Sensor
Sandia National Laboratories
Albuquerque, New Mexico USA

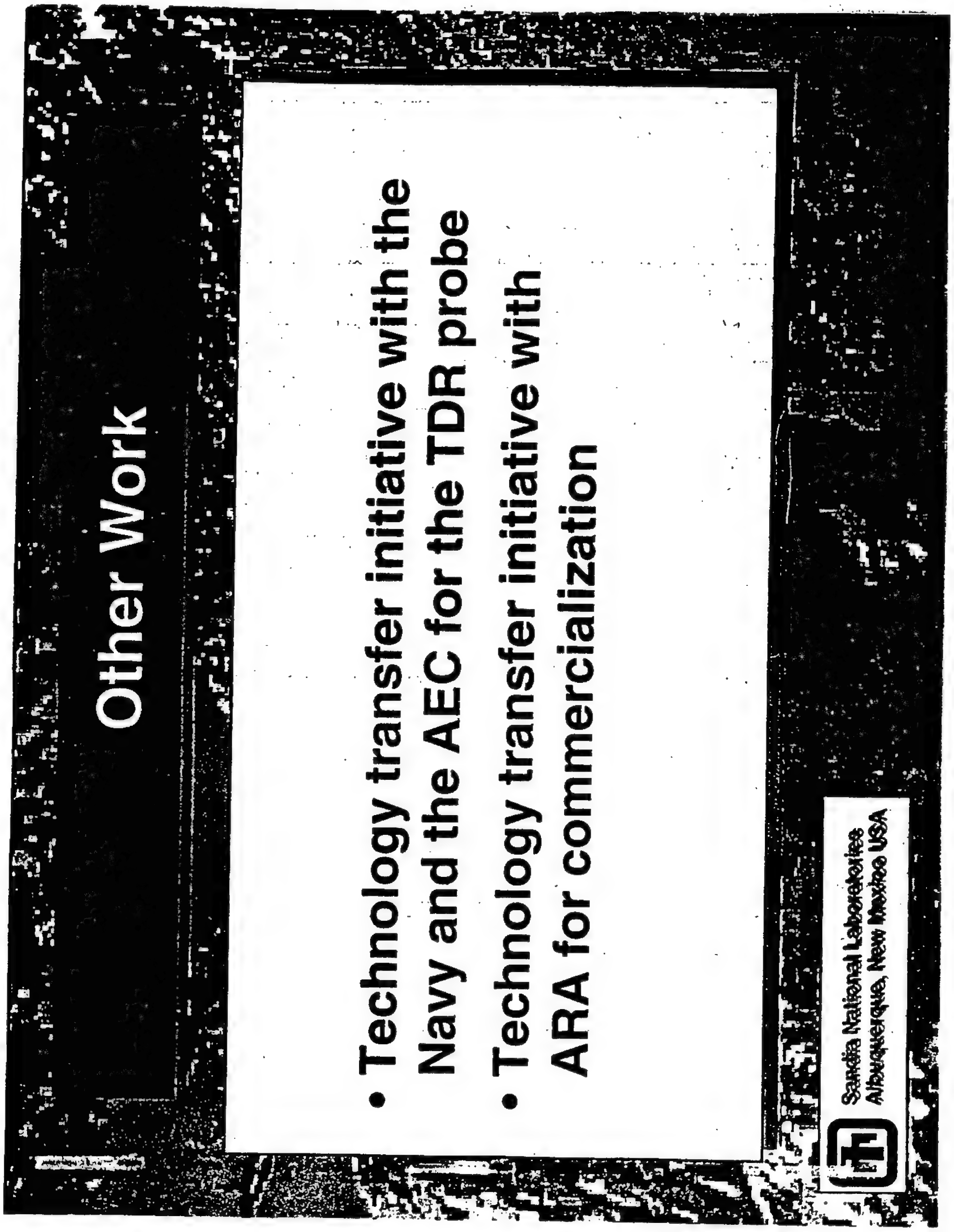

Results of Cone Penetrometer Testing of Sandia's TDR Moisture Probe
Sandia National Laboratories
Albuquerque, New Mexico USA


Area 1 Cone Penetrometer
Push Locations
C'
P9
A'
P5
P3
P8
Infiltration barrier
P7
B'
A
P4
B
P6
C
0'
5'
Sandia National Laboratories
Albuquerque, New Mexico USA



Area 1 Subsurface Geology
and Moisture Content
Sandia National Laboratories
Albuquerque, New Mexico USA


Moisture Content (theta)
0.0
Depth
37.0
31.0
Y
0.0
X
43.0
0.0
theta
5.560
38.14
Opaque from 15.01 to 38.14
Sandia National Laboratories
Albuquerque, New Mexico USA


Other Work
• Technology transfer initiative with the Navy and the AEC for the TDR probe
• Technology transfer initiative with ARA for commercialization
Sandia National Laboratories
Albuquerque, New Mexico USA

Field Testing at Two Sites

- South Royalton, VT at ARA facilities, 10/94
- Albuquerque, NM at Sandia National Laboratories, 11/94

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Conclusions

- TDR probe met or exceeded expectations for a real-time moisture content sensor
- Fiber optic capillary pore pressure sensor was successful in accuracy and precision, but less than desirable on equilibration time
    - Recommend for use in long-term spot measurements or as a monitoring device

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Fiber Optic IR Cone Penetrometer for Site Characterization

A research and development program funded by the U.S. Army Environmental Center

Sponsor: Mr. George Robitaille, AEC

Participants:
Naval Research Laboratory - Washington
- Dr. Ish Aggarwal (PM)
- Dr. Frank Bucholtz (PI)

US Geological Survey
Army Waterways Experiment Station

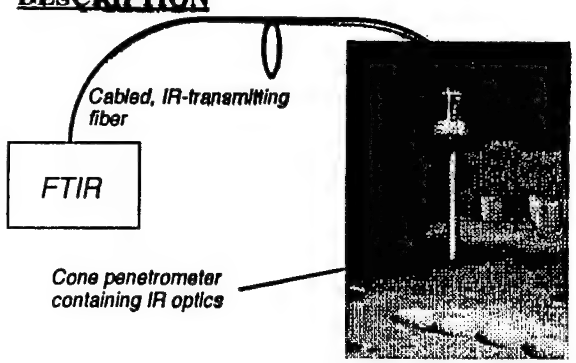
OBJECTIVES

- Develop fiber optic sensors to provide remote, in-situ detection of hydrocarbon contamination in soil for screening and characterization of environmental sites.
- Perform field tests in conjunction with SCAPS .

APPROACH

- Integrate infrared optics, FTIR spectroscopy and newly-developed IR transmitting chalcogenide fibers to produce a field-ruggedized sensor system.

DESCRIPTION

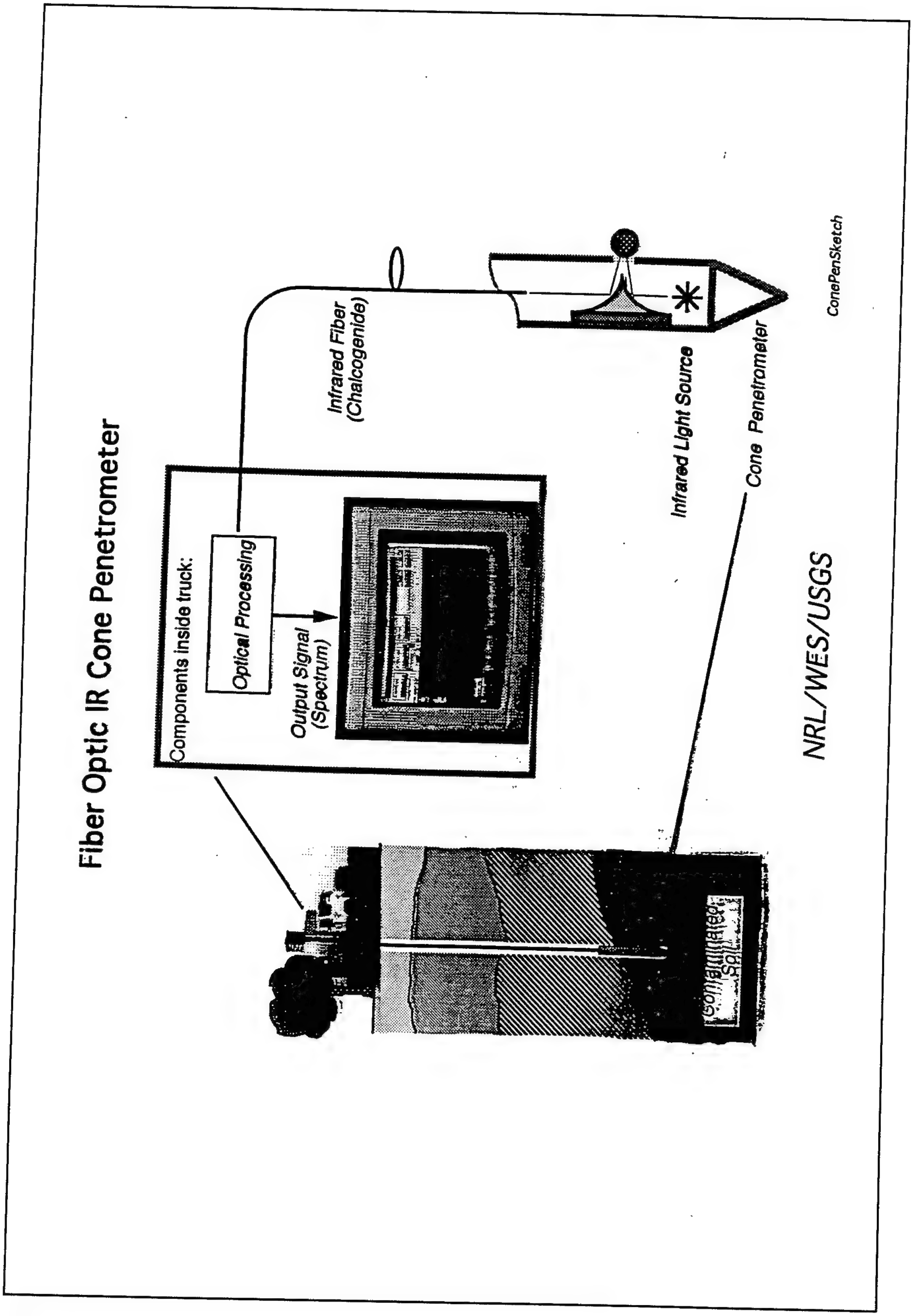


DELIVERABLE

- IR fiber optic sensor system for in-situ detection of hydrocarbon contaminants in soils.

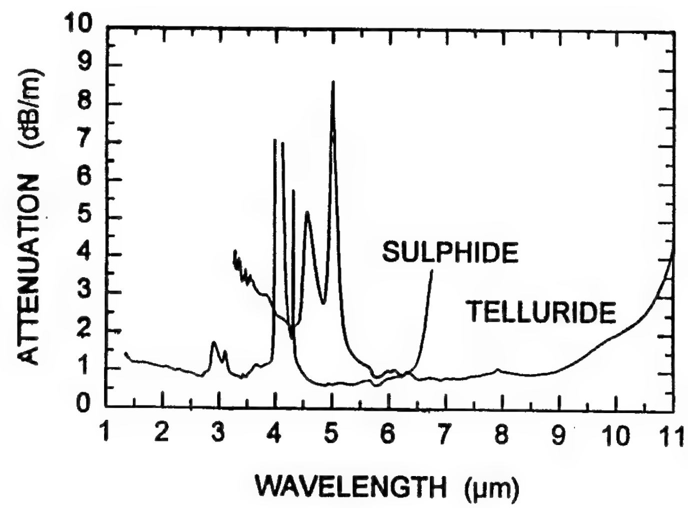
950710ia.chemquadchart

Naval Research Laboratory



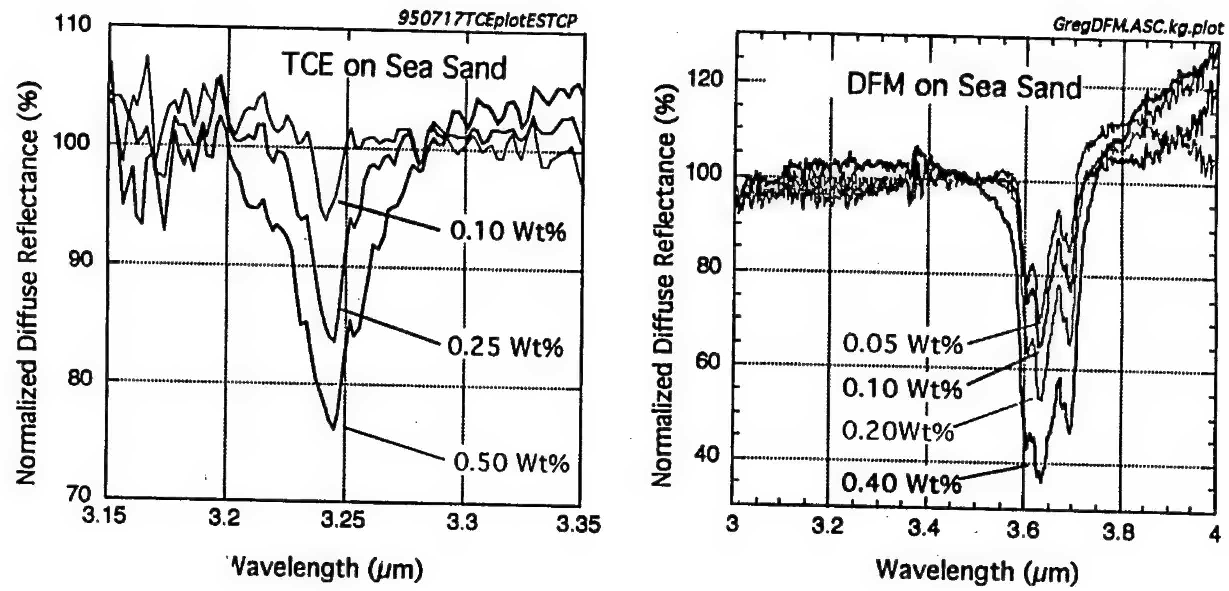
Fiber Optic IR Cone Penetrometer
Components inside truck:
Optical Processing
Output Signal (Spectrum)
Infrared Fiber (Chalcogenide)
Infrared Light Source
Cone Penetrometer
ConePenSketch
NRL/WES/USGS
Soil

GLASS CLADDED FIBERS



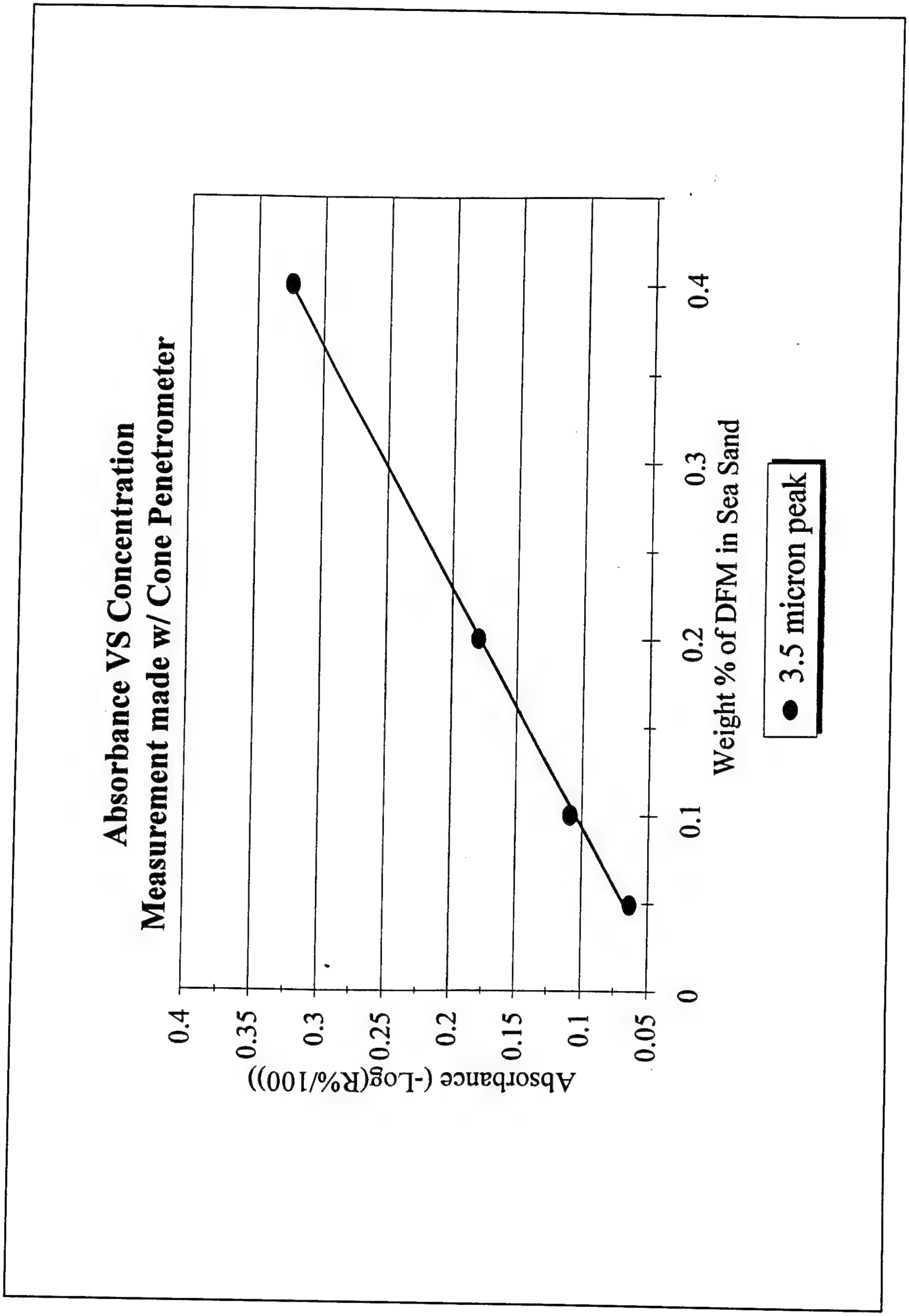
Fiber Optic IR Cone Penetrometer

Laboratory Measurements



950718 ESTCP02

NRL/WES/USGS


Absorbance VS Concentration
Measurement made w/ Cone Penetrometer
Absorbance (-Log(R%/100))
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0.1
0.2
0.3
0.4
Weight % of DFM in Sea Sand
3.5 micron peak

SUMMARY

Pre-Dover Laboratory Results on Cone Penetrometer System

Contaminant	Conditions	Detection Limit (ppm)
DFM	SAND, Large Sample, No fiber	50
DFM	SAND, Penetrometer, Cabled fiber	200
TCE	SAND, Large Sample, Cabled fiber	200

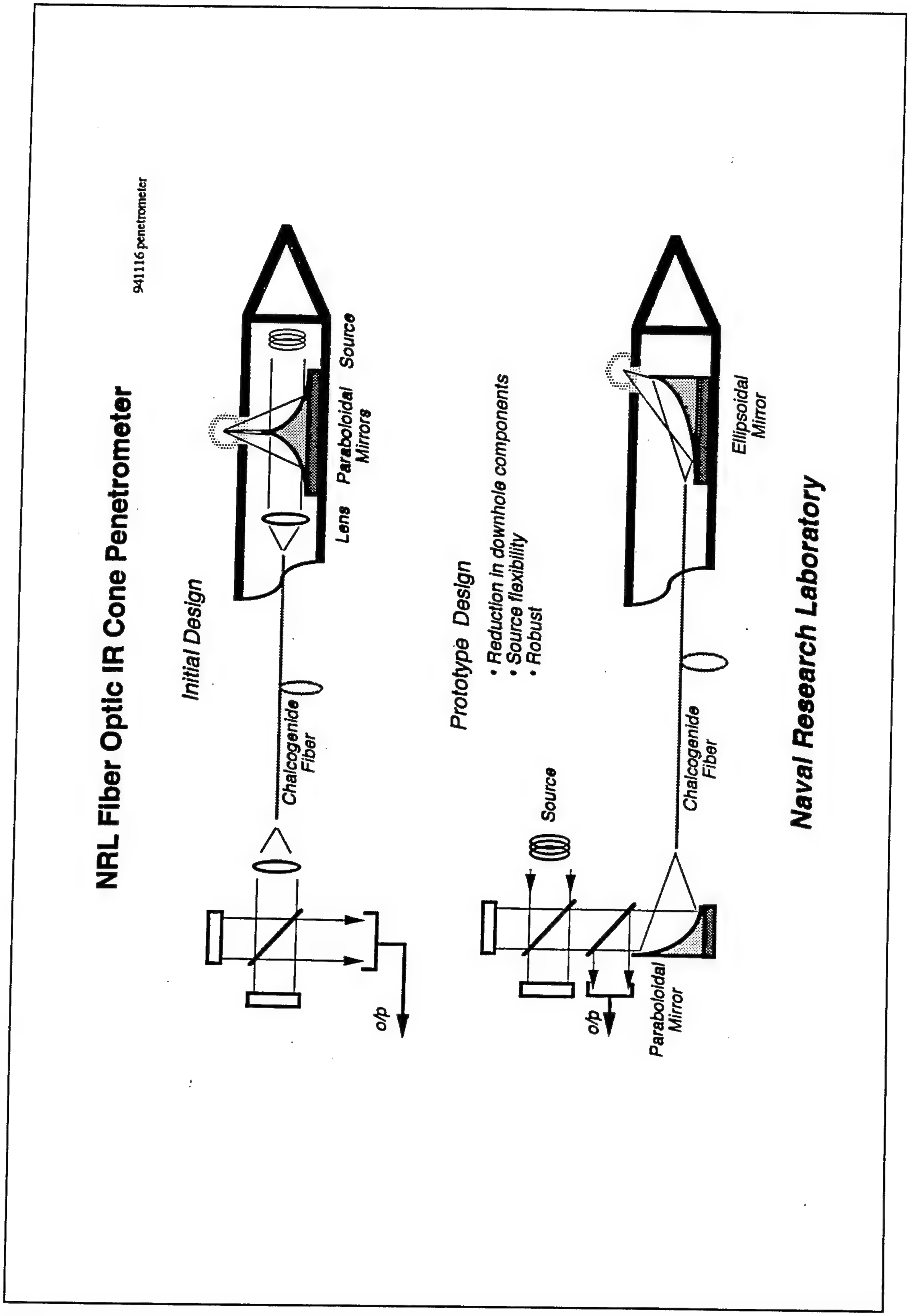
950707 pre-D

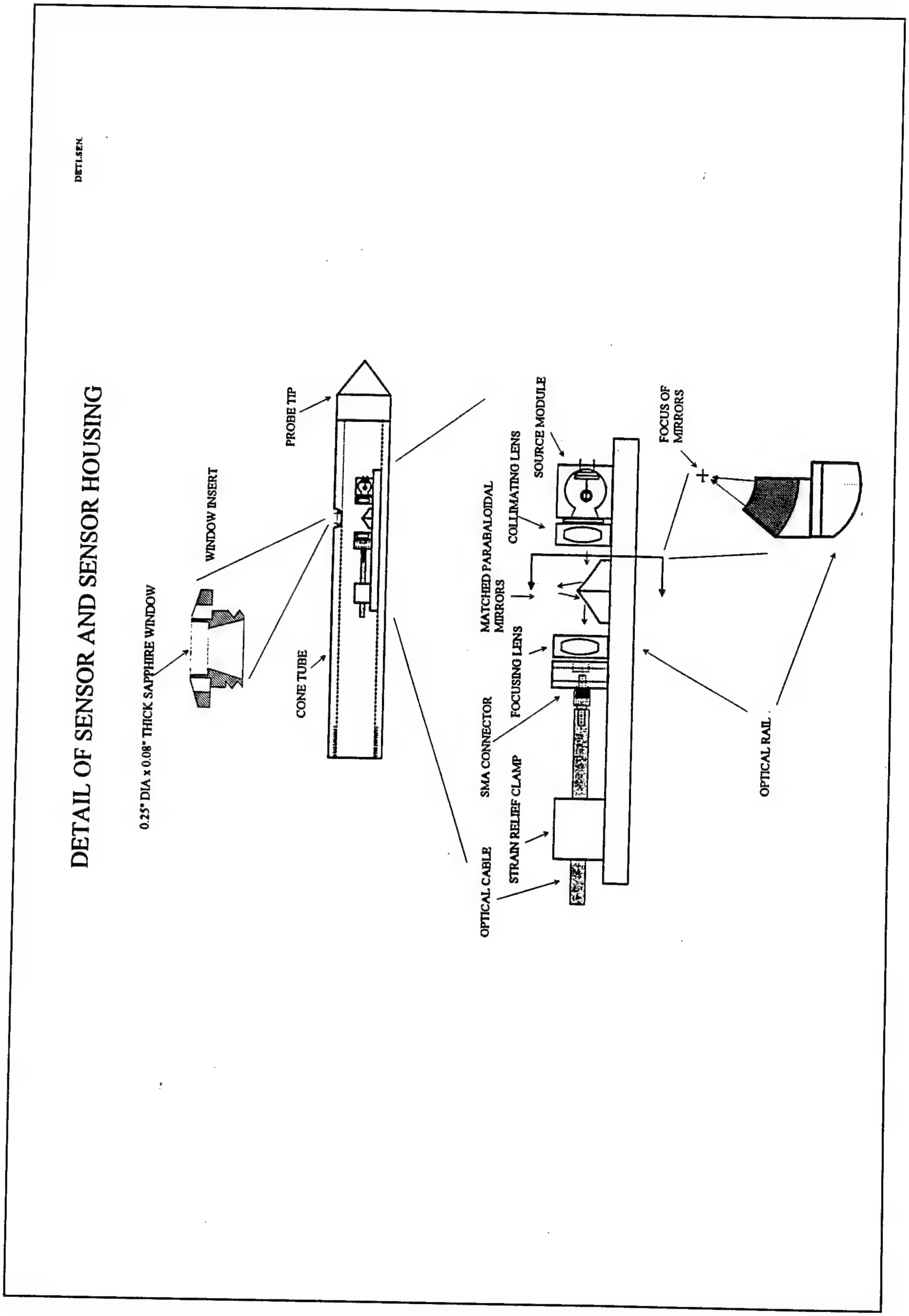
TECHNICAL ISSUES

Pre-Fabrication Stage (Fall '94)

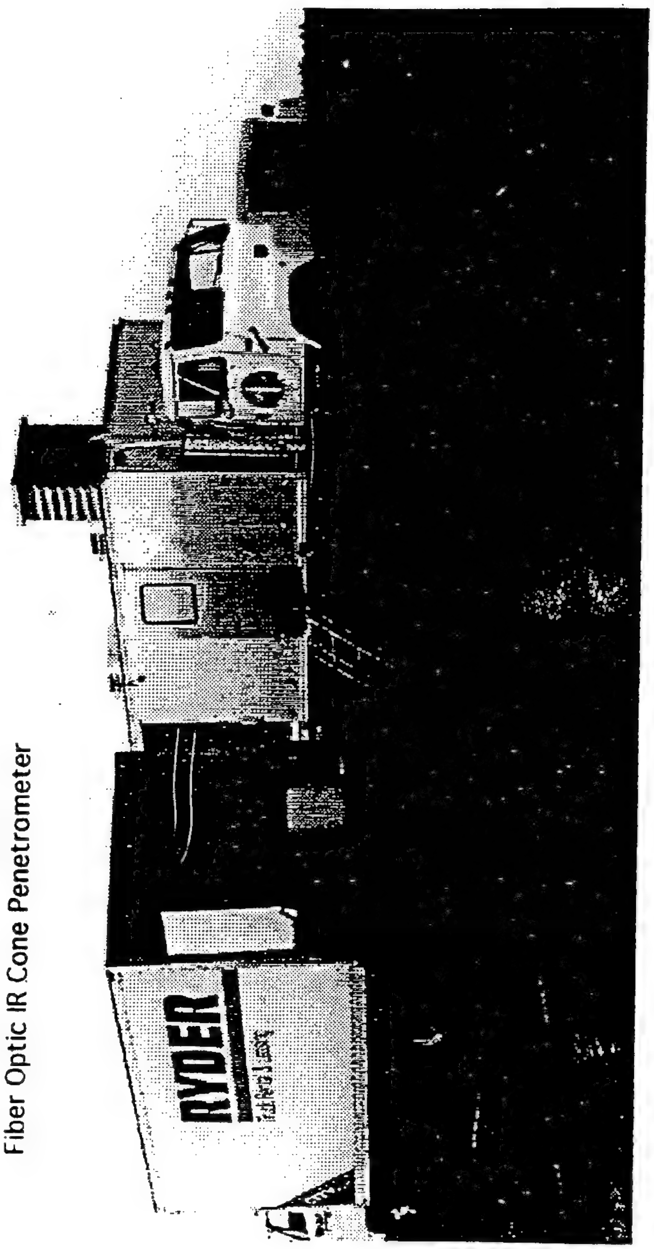
1. Miniaturization of optics
    - Reduction in optical throughput
    - Custom fabrication
2. Robustness of chalcogenide fiber cabled to useful lengths
3. Ruggedness and modularity of system (downhole optical rail, topside spectrometer)
4. Suitability of downhole source
    - Reliability
    - Effect of increased temperature on fiber, optics

950707 techissues


NRL Fiber Optic IR Cone Penetrometer
941116 penetrometer
Initial Design
Chalcogenide Fiber
Lens
Paraboloidal Mirrors
Source
o/p
Prototype Design
• Reduction in downhole components
• Source flexibility
• Robust
Source
Chalcogenide Fiber
Ellipsoidal Mirror
Paraboloidal Mirror
o/p
Naval Research Laboratory

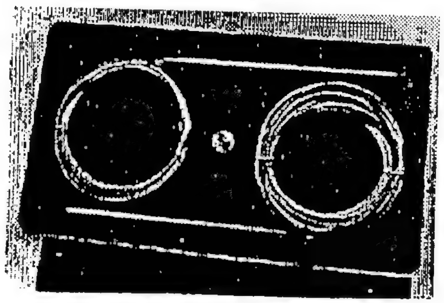

DETAIL OF SENSOR AND SENSOR HOUSING
DETI.SEN.
0.25" DIA x 0.08" THICK SAPPHIRE WINDOW
WINDOW INSERT
PROBE TIP
CONE TUBE
OPTICAL CABLE
STRAIN RELIEF CLAMP
SMA CONNECTOR
FOCUSING LENS
MATCHED PARABALOIDAL MIRRORS
COLLIMATING LENS
SOURCE MODULE
FOCUS OF MIRRORS
OPTICAL RAIL

DAFB Field Test May '95
Fiber Optic IR Cone Penetrometer

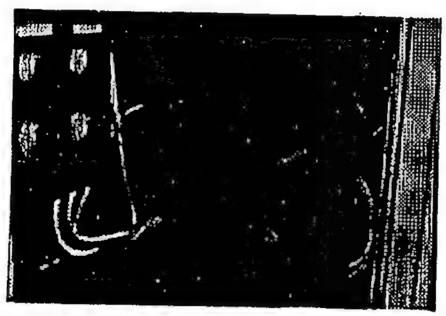


Fiber Optic IR Cone Penetrometer

Hardware and Performance



Two probes with cables attached



Cabled, IR-transmitting fiber on rack in SCAPS truck

Summary: Boyer AFB Field Test, May 1995

- Quick set-up (<1 hr)
- All hardware performed properly
- No failure/breakage in IR fiber cable during normal handling and operation in SCAPS

Performance of cabled IR fiber

Wavelength range of operation: 1.5 - 5.5 μm*

Total Optical Throughput (all wavelengths)
Field vs Lab: > 90%

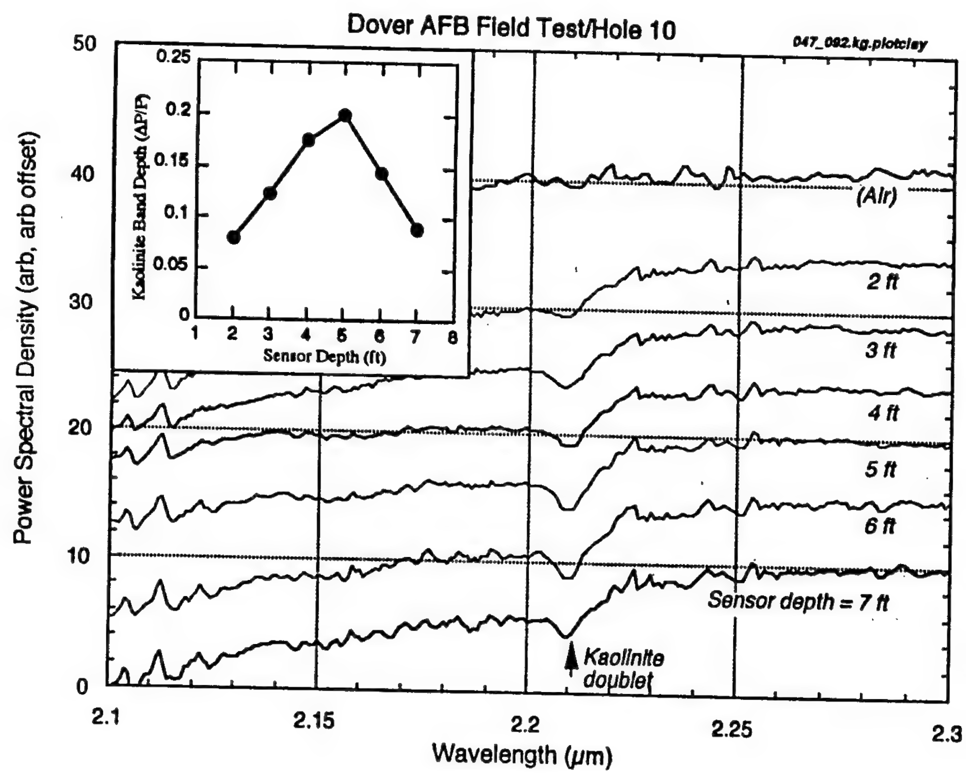
** FLimited by bulk optical components. Fiber itself extends to ≥ 10 μm.*

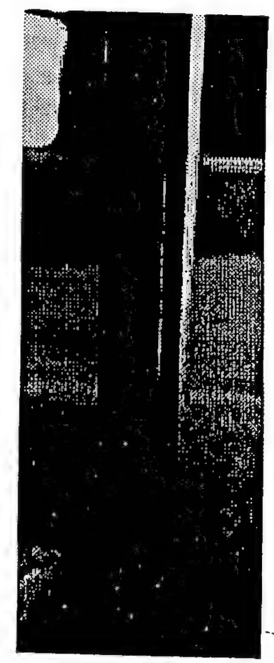
NRL/WES/USGS

950718 ESTCP04

Fiber Optic IR Cone Penetrometer

Field Result: Observation of Kaolinite (Clay) Absorption Band

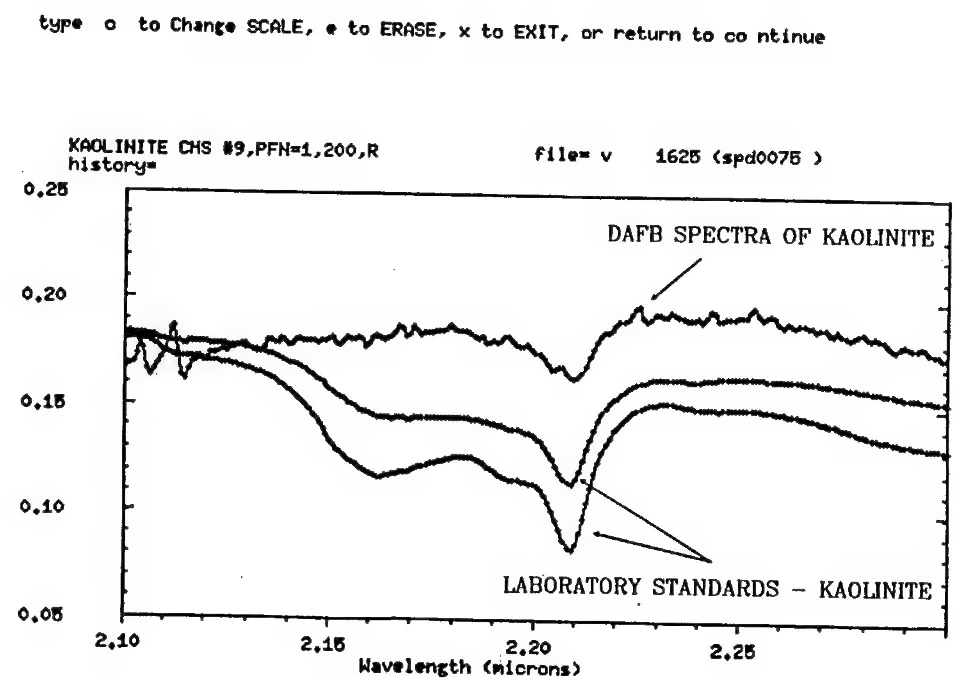




NRL/WES/USGS

SPIE.kaoplot.ESTCP

USGS COMPARISON OF SPECTRA FROM DAFB WITH
TWO LABORATORY STANDARDS OF KAOLINITE.



SUMMARY of TEST RESULTS
DAFB Field Test, May 1995

Demonstrated rugged sensor system comprising IR-transmitting fiber cable, cone penetrometer optics, and spectrometer.

- Quick set-up (< 1 hr)
- Harware functioned properly
- No special cable handling required
- Optics continued functioning after penetrometer tube was bent

Successfully observed kaolinite (clay) absorption spectra & variation of absorption band with depth & location

Hydrocarbon bands not observed due to combination of low/unknown concentration levels and remaining technical issues:

- Low soil albedo compared to background
- Competing absorption bands in soil, optics (H20, HS)
- Interfering hydrocarbon bands

950707 summtest

PROPOSED SYSTEM IMPROVEMENTS
(Based on Dover AFB Field Test Results)

Technical Issue	Solution
• Low soil albedo compared to background	• Improve optical throughput (x 25 expected) • *7-Fiber bundle* • *CPC collector mirror* • *Paraboloidal exit mirror* • *AR coating*
• Competing absorption bands	• Replace KBr optics with CaF_2, ZnSe optics • Improve fiber materials • Improve purge system
• Interfering hydrocarbon bands	• Reduce CH contamination in fiber & optical system

950707 improv

IR PROBE COLLECTION OPTICS ENHANCEMENT

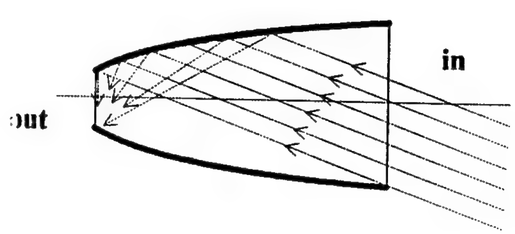
COMPOUND PARABOLIC CONCENTRATOR (CPC)

TRADE AREA FOR NA

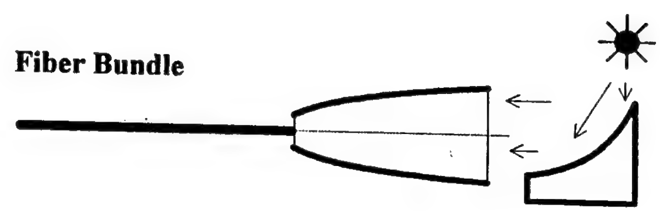
ALLOWS FOR CLOSE TO THEORETICAL MAXIMUM
CONCENTRATION OF INCOMING RADIATION (NA OUT =1)

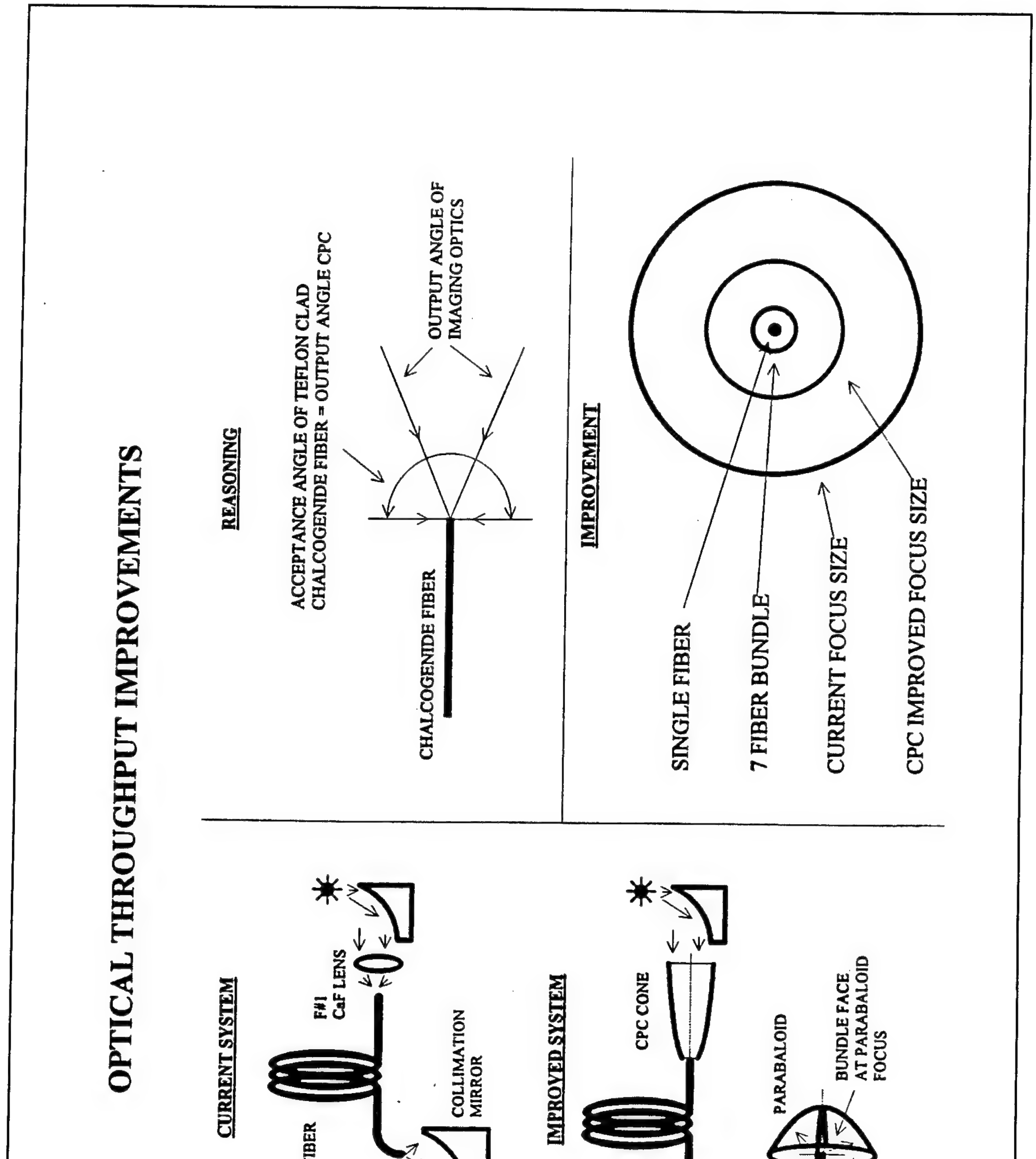
Cmax = (1/SIN[THETAin])^2

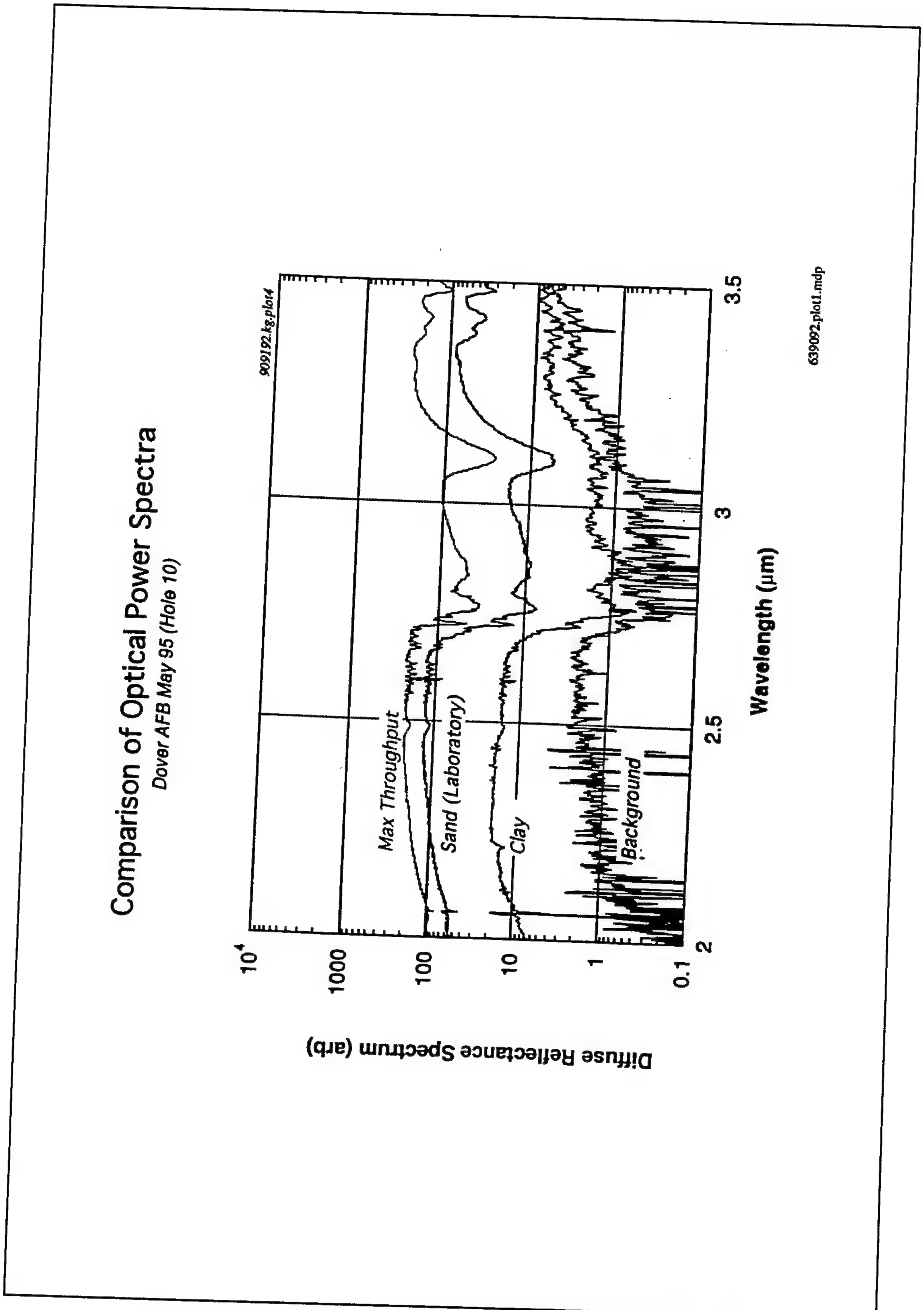
CPC OPERATION



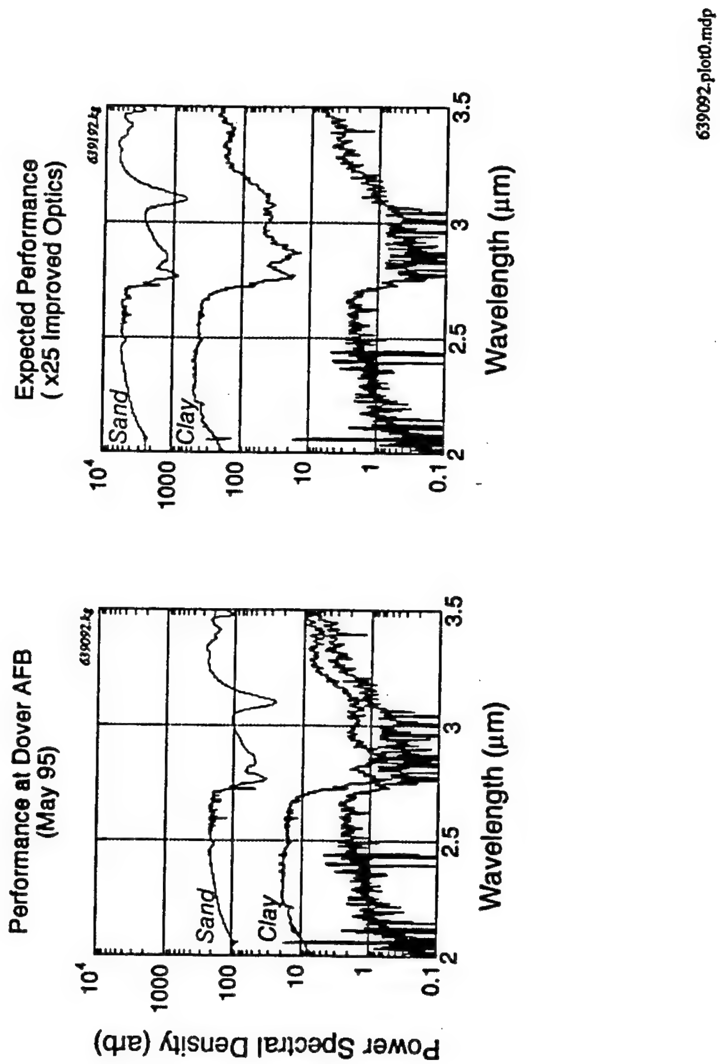
NEW COLLECTION SYSTEM

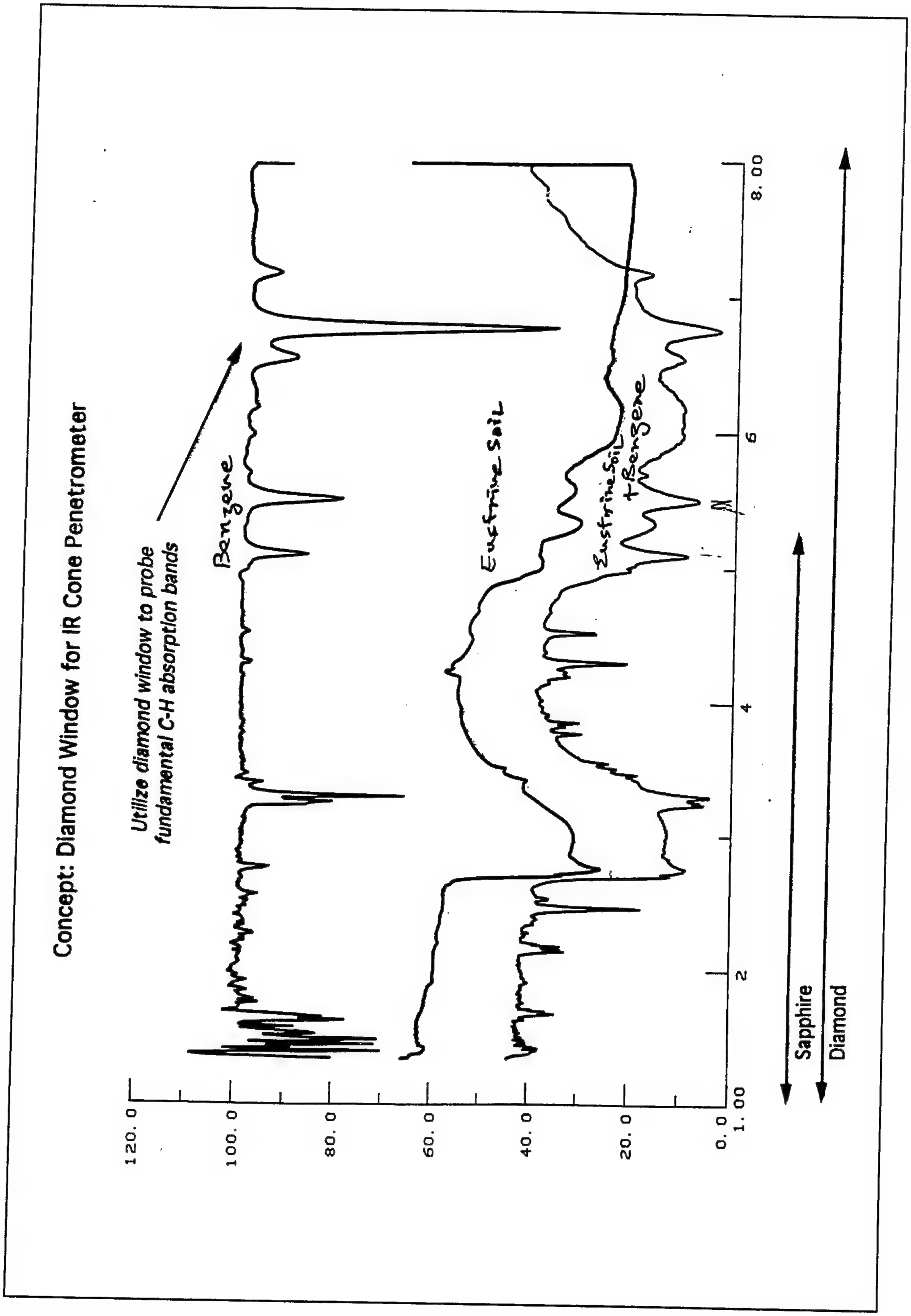



OPTICAL THROUGHPUT IMPROVEMENTS
CURRENT SYSTEM
F#1
CaF LENS
OPTICAL FIBER
BUNDLE
COLLIMATION
MIRROR
FTIR
ENTRANCE
PORT
IMPROVED SYSTEM
CPC CONE
FIBER BUNDLE
PARABALOID
BUNDLE FACE
AT PARABALOID
FOCUS
FTIR
ENTRANCE
PORT
REASONING
ACCEPTANCE ANGLE OF TEFLON CLAD
CHALCOGENIDE FIBER = OUTPUT ANGLE CPC
OUTPUT ANGLE OF
IMAGING OPTICS
CHALCOGENIDE FIBER
IMPROVEMENT
SINGLE FIBER
7 FIBER BUNDLE
CURRENT FOCUS SIZE
CPC IMPROVED FOCUS SIZE


Comparison of Optical Power Spectra
Dover AFB May 95 (Hole 10)
Diffuse Reflectance Spectrum (arb)
Wavelength (µm)
10^4
1000
100
10
1
0.1
2
2.5
3
3.5
Max Throughput
Sand (Laboratory)
Clay
Background
909192.kg.plot4
639092.plot1.mdp

Comparison of Current and Improved Performance

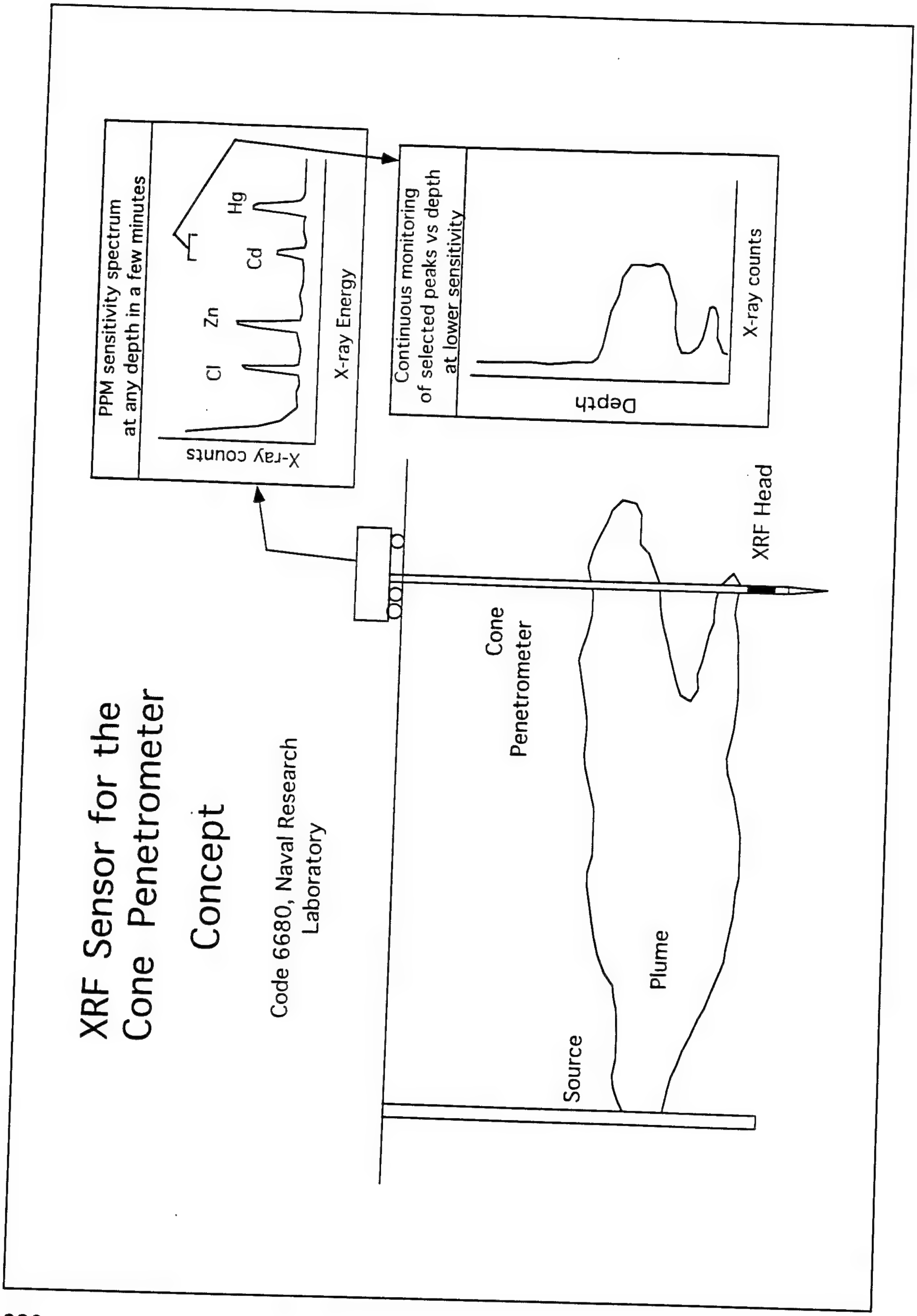



Concept: Diamond Window for IR Cone Penetrometer
Utilize diamond window to probe fundamental C-H absorption bands
Benzene
Eustrine Soil
Eustrine Soil + Benzene
120.0
100.0
80.0
60.0
40.0
20.0
0.0
1.00
2
4
6
8.00
Sapphire
Diamond

Metals Detection with an XRF Sensor for the Cone Penetrometer

W. T. Elam
Naval Research Laboratory
Code 6685
Washington, DC 20375-5345

30 August 1995



XRF Sensor for the Cone Penetrometer
Concept
Code 6680, Naval Research Laboratory
PPM sensitivity spectrum at any depth in a few minutes
X-ray counts
Cl
Zn
Cd
Hg
X-ray Energy
Continuous monitoring of selected peaks vs depth at lower sensitivity
Depth
X-ray counts
Cone Penetrometer
XRF Head
Source
Plume

XRF Sensor for the Cone Penetrometer

Requirements

must fit penetrometer geometry
- small diameter (max. 2 inch O. D.)
- rugged construction
- strong x-ray window

detect all metals $Z>20$ (scandium)

Detection limits well below 100 ppm
- (field screening)

100 or less second data collection times
- (approx. time required for penetrometer ram retraction)

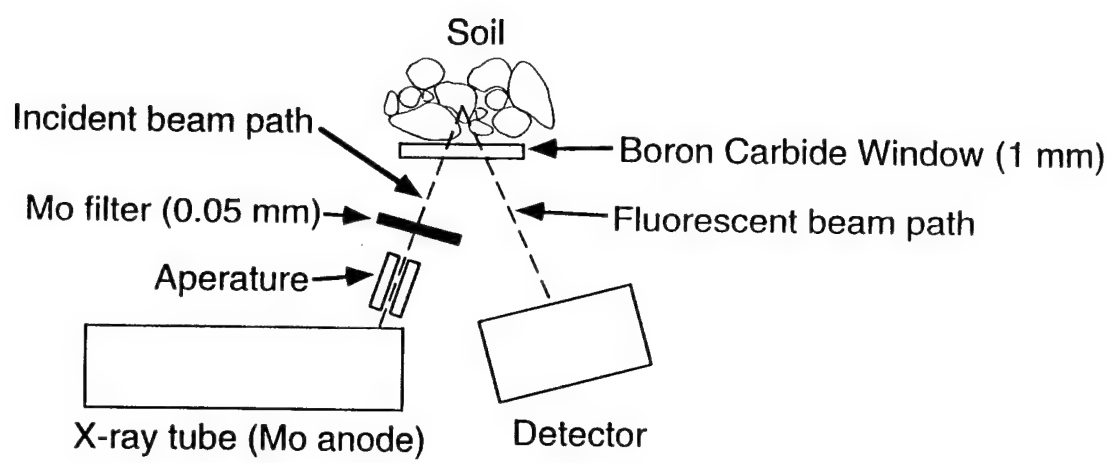
XRF Sensor for the Cone Penetrometer

Sub-Systems

Below Ground	Cables	Above Ground
X-ray Source	High Voltage	X-ray Source Power Supply
Collimators	Signal	Detector Amplifier and Pulse Shaping
Window	Power	Interlocks
X-ray Detector	Shields and Grounds	Multi-Channel Analyzer
Preamp		Data Reduction
Mounting Platform		Display
Heat Dissipation		Interface to Penetrometer Truck

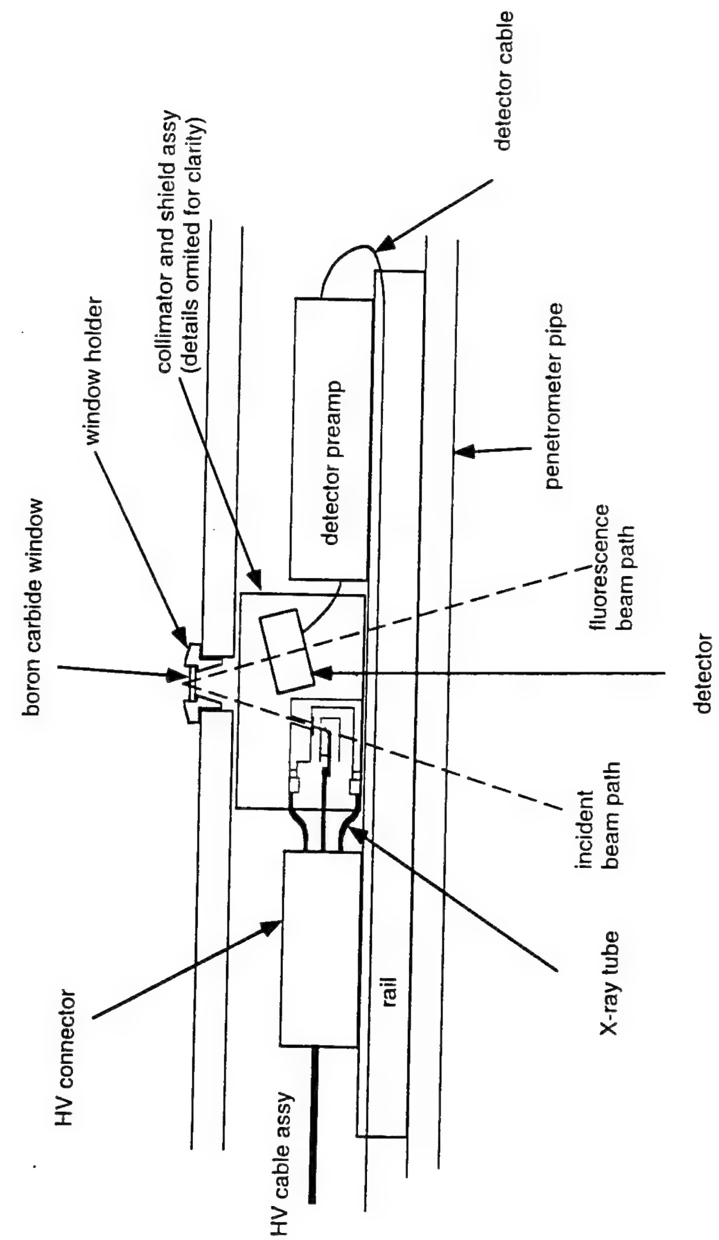
XRF Sensor for the Cone Penetrometer

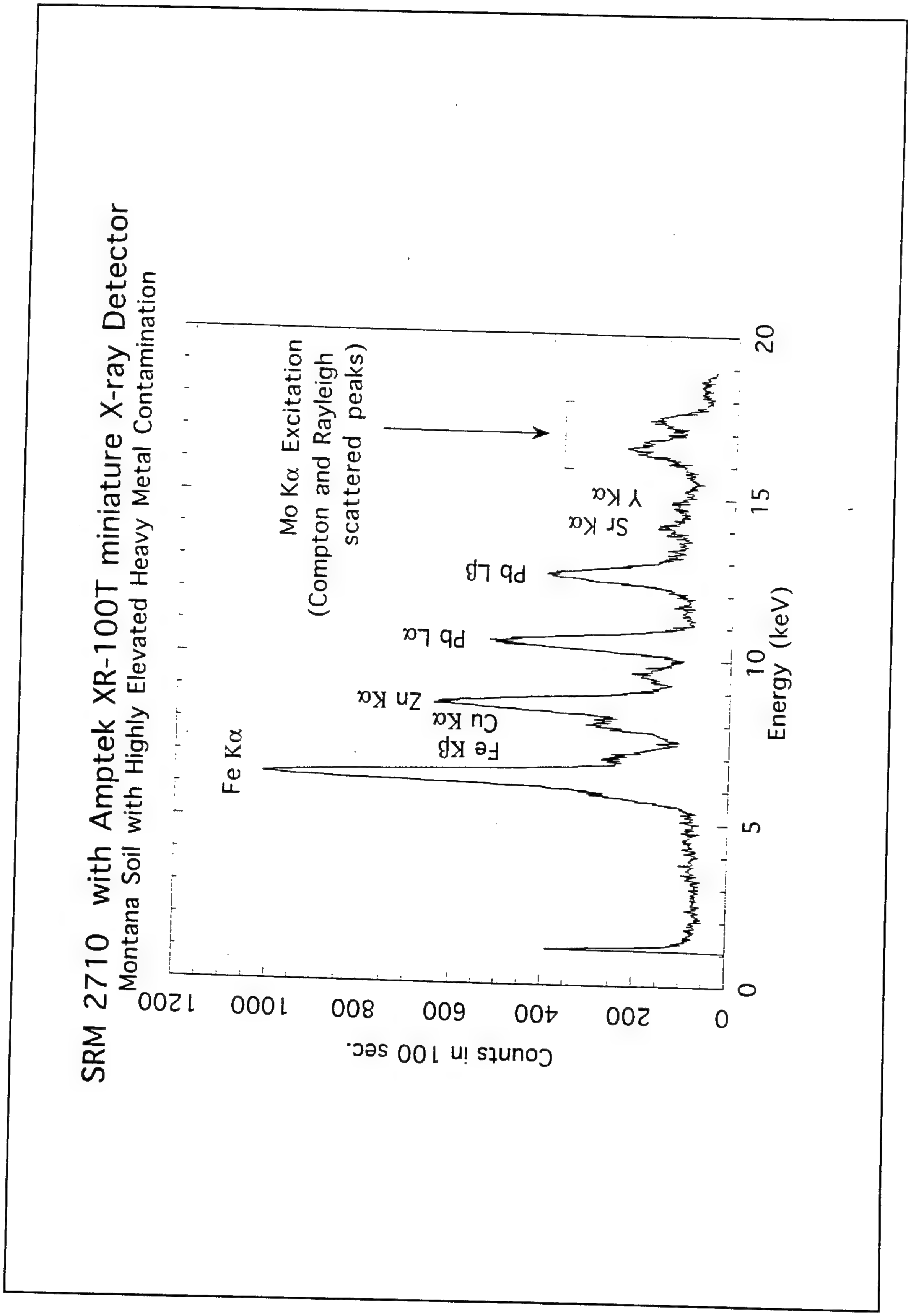
X-ray Optics Layout



XRF Sensor for the Cone Penetrometer

Engineering Layout




SRM 2710 with Amptek XR-100T miniature X-ray Detector
Montana Soil with Highly Elevated Heavy Metal Contamination
Counts in 100 sec.
Energy (keV)
Fe Kα
Fe Kβ
Cu Kα
Zn Kα
Pb Lα
Pb Lβ
Sr Kα
Y Kα
Mo Kα Excitation
(Compton and Rayleigh
scattered peaks)

XRF Sensor for the Cone Penetrometer

X-ray Tube Requirements

Critical requirements:

- Molybdenum anode
- Maximum operating voltage 35 kV (continuous)
- Maximum operating current 0.5 ma (continuous)
- Maximum operating power 18 watts (continuous)
- Cooling via contact with housing
- Maximum length 6 inches
- Focal spot approximately 0.080 inch (2 mm) diameter or less
- *Maximum diameter 0.625 inches (15 mm) at any point on length*

XRF Sensor for the Cone Penetrometer

Prototype Development Timeline

Assemble Sensor	October 1995
Obtain Performance Data (especially detection limits)	March 1996
Field Test of Sensor	Summer 1996

XRF Sensor for the Cone Penetrometer

Requirements and Status

(as of August 1995)

Detector	On hand, tested
Re-mounted preamp	In progress
Boron Carbide Windows	Received and mounted, testing in progress
Mounting rail	On hand
X-ray tube	Vendor selected, order in progress
Structural Components	Final design waiting on x-ray tube design
Collimators	
Window holder	
Pipe section	

9 SERDP Peer Review Panel Conclusions and Recommendations

The peer review panel members raised questions and made comments throughout this workshop. The panel members were asked to submit their written comments to the workshop coordinator to be included in these proceedings. The following comments were submitted in memorandum form and have not been altered.

MEMORANDUM FOR THE RECORD

SUBJECT: Second Annual SCAPS Sensor Development Workshop

FROM: Jeff Marquesee

DATE: August 31, 1995

The annual Tri-Service SERDP SCAPS program review was held at Waterways Experiment Station August 29 and 30. The SCAPS Tri-Service funding profile from SERDP and other DoD sources is shown below.

	FY94 $K	FY95 $K	FY96 $K	FY97 $K
SERDP	3,375	1,060	1,790	2,350
Non-SERDP	2,641	2,580	850	350
Total	6,016	3,640	2,640	2,700

In addition to these funds, ESTCP and Navy DERA have provided funding for the demonstration and validation of SCAPS technology.

The SERDP Science Advisory Board requested that the program be reviewed by an independent peer review group every year. The review committee consisted of:

Dr. Jeffrey Marquesee, DoD
Mr. Eric Lightner, DOE
Dr. Greg Rosasco, NIST
Dr. Carl Enfield, EPA

The review covered the seven areas currently receiving SERDP funding. They are:

1. Laser Induced Breakdown Spectroscopy
2. Laser Induced Fluorescence Sensors: POL and Explosives
3. Fiber Optic Raman Sensors
4. Electrochemical Sensors: Explosives and VOCs
5. Spectral Gamma Probe
6. Sampling Technology
7. Data Processing Methodologies
8. Technology Demonstration

Details on these seven topics are available.

Attached are my comments and recommendations provided to the program manager regarding the ongoing SERDP funding work.

Comments on SERDP Funded SCAPS Development

General

- Overall, the work is important to the DoD and addresses real user needs. The quality is high and support should be maintained.

- For successful execution, tri-service participation is essential. Although the SCAPS program's level of tri-service cooperation is far beyond other environmental programs, improvements in coordination are still needed. In particular, the work being performed by the Air Force is not being coordinated sufficiently with the ongoing Army and Navy work.

- SCAPS clearly addresses a specific user defined requirement. The earlier development of the POL LIF sensor had close interaction with the user community. The current sensor development needs to maintain a high level of user interaction to assure that these sensors will provide operational capabilities needed by the DoD cleanup community. It is recommended that on a sensor/contaminant basis the developers meet with members of the user community and obtain appropriate feedback.

- The current review was limited to government participants. It is recommended that in the future the non-government groups involved in the SERDP funded R&D be invited.

- It is recommended that the program maintain its short term focus on providing the user community with near term technologies that can be used for screening the condition of a contaminated site. The current approach of simultaneously looking at multiple technical approaches to address a single problem should be maintained in order to move the technology to the field rapidly. While maintaining this near term focus, SERDP should also consider supplementary efforts to exploit the potentially more quantitative nature of these sensors. In the out years, the user community will have an increasing need for characterization tools that can monitor the progress of ongoing remediation activities. The value of a quantitative measurement of the ratio of various aromatic compounds by LIF would be high, even if the absolute scale for an individual compound cannot be determined.

- The role of field testing and demonstrations is important. The ongoing work under SERDP funding appears to be of mixed quality and at times unfocused. With increased support planned for these activities in FY96, it is important that the objectives of the various field tests be clearly defined.

Below are additional comments on the specific areas briefed.

<u>Laser Induced Breakdown Spectroscopy</u>

The work in this area has a great potential payoff and support should be maintained at a high level to assure a rapid transition to the field user.

<u>Laser Induced Fluorescence Sensors</u>

<u>POL</u>

- The ongoing work at NRaD is of high quality with an excellent short term focus on providing opportunities for technology insertion into existing systems.

- The lasers being provided by MIT/LL offer a great potential and should be fully exploited to determine their value.

- The work described by the Air Force and Navy appears uncoordinated and potentially duplicative. A coordinated program needs to be constructed.

- The Air Force work appears to be supporting one commercialized approach and overlaps the TRP funded work in this area.

Explosives

- There is great need for a sensor which could cost effectively and rapidly map out explosive contaminants in groundwater. This sensor is advertised as having that potential.

- The current effort appears to be funded at such a low level that it is below the critical mass needed to really advance the technology. The measurement approach needs to be pushed in the lab to answer the basic questions on feasibility followed by a decision to either drop support or significantly increase support.

- It is recommended that in the near term, lab experiments be performed to determine if this technology can detect explosives in the soil, then the focus must move to determine if there is a potential to differentiate between NO from explosives vs. NO from fertilizer sources that widely contaminant groundwater in the U.S. If there is no potential for differentiating these two sources then the user community in the Army needs to be queried on the potential value of such a sensor.

Fiber Optic Raman Sensors

- The Navy work briefed clearly showed the shortcomings of this approach. The work was high quality even if the resulting answer is a disappointment.

- The Navy is currently altering their work to look at surface enhanced Raman for a detector of DNAPL. Before proceeding with this project, it is recommended that the Navy assess whether such a technically sophisticated sensor is really the best approach if it will only be able to detect free product and if the market will support such a sensor.

- Given the recent results of the Navy, the current Air Force plans are not well justified. The work proposed is not clearly leading to an advancement, which will provide a new operational capability.

Electrochemical Sensors: Explosives and VOCs

- These sensors represent good near term products that should be transitioned to the user rapidly.

Spectral Gamma Probe

- This work does not address a DoD requirement. It is recommended that SERDP support for this work be discontinued.

Sampling Technology

- The thermal desorption sampling is an excellent tool that should be transitioned rapidly. The future SERDP work should focus on questions associated with its operational use; i.e., developing an appropriate protocol for field use to assure an accurate sample is collected.

- The multi-port sampler results were inconsistent. The modeling proposed to understand the results will not fully address the important questions. It is recommended that additional experimental work be performed to identify the cause of the anomalous results.

<u>Data Processing Methodologies</u>

- It is recommended that this effort be decreased in the out years. The work presented appeared to be of good quality, but SCAPS should exploit and rely on existing commercial software to the maximum extent possible.

<u>Technology Demonstration</u>

- The planned demonstrations conducted by the Services require greater coordination.

- The value and expended product for each field test should be explicitly defined prior to initiating any extensive field activities.

SCAPS Technical Peer Review -- August 29-30, 1995
Report of Greg Rosasco, NIST

General comment:

As discussed at the time of the meeting, it would be most helpful for the purposes of such a review to provide an overall roadmap which provides the rationale for the technical program for each of the technologies presently encompassed by the SERDP sensor acceleration funding. This roadmap would provide a brief description of the measurement problem, e.g., POL contamination characterization, the critical requirements of the measurement system, e.g., detection and relative quantitation at the sub 400 ppm level in the vadose or water table level for the following compounds in an asserted priority order. The problem definition should give some sense of user priority and critical measurement needs, both within an area, e.g., energetic compound detection, and between areas, e.g., relative importance of heavy metal detection vs. POLs or explosives. The problem definition would be followed by a brief assessment of the current state-of-the-art in sensor technology to address this problem, this should logically set the rationale for the SERDP funded effort. Within each technology selected for acceleration, critical decision points, accomplishment and time schedules, should be identified to understand the decisions as to continuation, expansion, cessation, incorporation in penetrometer test, etc. The comments with regard to "not understanding how the AF portion of the effort fit into the overall strategy" I think were engendered by this lack of clear understanding of the bigger picture. This not to say that such a roadmap or plan doesn't exit, but rather that the review team could not discern the plan in the time allowed for the review.

Individual program areas:

LIBS: An innovative, highly promising approach which, if rapidly incorporated in survey studies, could greatly add to the understanding of heavy metal contamination, transport, and remediation. Since the fiber optic transmission of the receiver is better than 20 percent for wavelengths above 330 nm, some evaluation of the ability to detect Cd and Zn for longer wavelengths should be tested in the lab. The likelihood that the AOTF-PMT down-hole detector approach will provide analytically significant data (in the 220 nm region or any other spectral region) in time to incorporate the technology into the SCAPS system does not appear to be high. The inherent irreproducibility of the spectrum on a shot-to-shot basis suggests that the only useful normalization will come from simultaneous multielement comparisons available from the currently practiced multichannel spectroscopy approach. The downhole, high energy Nd:YAG system seems ideal (even if the rep rate is low). Some focus adjustment may be required to optimize plasma generation depending on soil type; as an alternative to the current design for the probe, one could imagine a small, 250 micrometer port which would allow access to the soil with a purge and dump area below it to allow any material that entered through the port to be expelled. The system seems very close to ready for field tests. Good work.

LIF for POL: Outstanding results, especially those related by Dr. Lieberman in his review of the Navy demonstrations in CA. The potentialities of the diode laser pumped downhole Nd:YAG laser are outstanding. If the system could be configured to allow wavelength selection, the range of excitation wavelengths would be remarkable, and thereby allow a tremendous number of tests, including wavelength optimization for Raman spectroscopy, which is after all, at least operationally, just off resonance fluorescence. The wavelength selection could include 808 nm from the diode, 1060 nm from the YAG, either of which might reduce fluorescence for Raman, (unfortunately one would have to use FT Raman analysis for the 1060 excitation). The 532 nm power would be useful for Raman excitation and would eliminate the current problems with the interfering silica Raman spectrum coming from the input excitation fiber in the current FORS system, this may allow mineral characterization and perhaps water content measurements, a subject of interest in general. The ability to switch to short wavelength excitation of the POLs may add the ability to do some relative quantitation of heavy and light fractions or aging, as discussed in the meeting. This is a first rate opportunity and should be pushed hard. No similar justification has been advanced for the dye system, the OPO, the powdered doubler or the Ti:Sapphire work. The explosives detection effort of Sausa should be funded at a sufficient level to allow a critical test of the possibilities of detection of the compounds of interest in the matrix of interest in the presence of the user identified interferants. No spectroscopy, simply see if a one photon, deep UV or a two photon, excitation detection scheme will give qualitative, analytically useful (perhaps for screening purposes) indication of the presence of the explosives.

FORS: The work to date is first rate, a sensible, "utilize the state-of-the-art approach" has been followed. Other than the suggestions above with regard to the potential of a downhole multiwavelength source, the near term utility of this system seems to have been evaluated. It is unfortunate that no data appear to have been taken in any part of the push, prior to failure in the one field test that was reported. There is still the question as to the utility of Raman spectroscopy to help distinguish the nature of the geological layer that the probe is passing through, as a supplement to the other, admittedly crude, characterizations available from the geotechnical stress/friction data. Although I am vaguely familiar with a SERS based enhancement of sensitivity for Raman spectroscopy, I think there are other extractive, trapping technologies available and better suited to the needs of SCAPS.

Electrochemical sensors: Ready for incorporation in the SCAPS system and should be subjected to complete validation tests in parallel with other such tests. Good work.

Spectral gamma: Subcritical effort, no further comment.

Sampling technology: This catalytically enhanced thermal desorption technique appears ready for field validation and deployment. Good work. The multiport sampler needs some more thought as to how to perform the validation studies, but it appears otherwise a mature technology for soil gas

sampling. I am not sure why one needs both the thermal desorption and the multiport to get soil gas, one could just turn off the heater in the retracted cone version of the thermal desorption sampler and have a means to sample a controlled volume for soil gas. This multiport sampler is mature, it does not need more SERDP acceleration funding.

Data processing methodologies: Should be incorporated as required in the transitioning of each technology into the SCAPS. It should not be a research area in itself.

Field Demonstrations: Some are just field tests, and these should be differentiated and included in the process of transitioning the technology into the SCAPS. The demonstrations at Dover and those conducted at Port Hueneme and North Island jointly with CAL EPA and the Western Governors Association were outstanding examples of what to do in a field demonstration. More sensors and more data should be obtained in such tests, since so much expense goes into the testing and supportive extractive analyses.

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References

Cespedes, E. R., Miles, B. H., and Lieberman, S. H. (1994). "Development of optical sensors for the Site Characterization and Analysis Penetrometer System (SCAPS)." *Proceedings of the International Specialty Conference on Optical Sensing for Environmental Monitoring Vol. SP89*, Air and Waste Management Association/SPIE, Atlanta, GA, 621-632.

Lieberman, S. H., Theriault, G. A., Cooper, S. S., Malone, P. G., Olsen, R. S., and Lurk, P. W. (1991). "Rapid subsurface in situ screening of petroleum hydrocarbon contamination using laser induced fluorescence over optical fibers." *Proceedings of the Second International Symposium on Filed Screening Methods for Hazardous Wastes and Toxic Chemicals*, Air and Waste Management Association, Las Vegas, NV, 57-63.

SERDP. (1995). "1995 Annual Report and Five-Year (1995-1999) Strategic Investment Plan," Arlington, VA, CU-4 - CU-9.

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13. ABSTRACT *(Maximum 200 words)*

The Second Annual Site Characterization and Analysis Penetrometer System (SCAPS) Sensor Development Workshop was held at the U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, during August 29 and 30, 1996. In attendance were researchers, managers, and SCAPS users representing the Army, Navy, Air Force, the Department of Defense, the Department of Energy, the Environmental Protection Agency, and the National Institute of Standards and Technology. Workshop participants presented briefings on the status of their SCAPS-related sensor research, development, and demonstration efforts. Managers and users of SCAPS technologies participated in the briefings and discussions and described the needs and concerns from the users' perspective. The Peer Review Panel evaluated the progress of the Tri-Service SCAPS sensor development project and presented recommendations for future work.

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